



## DECLARATION

I, Hartley Owen, am the inventor of the application described in US10/621,197 filed on 07/16/2003. I am the inventor or co-inventor of over 290 US patents, with numerous foreign patents. I have spent my professional career at Mobil in developing the catalytic cracking process. I am also the author of the paper "50 Years of Catalytic Cracking" Oil & Gas Journal, week of January 8, 1990, which reviews many of the problems and developments of this process.

I have reviewed the communications from Examiner Douglas, and the references cited against my application and wish to make several observations.

FCC units have been plagued with thermal cracking of vapors from the FCC stripper for decades. Most refiners choose to live with the problem, i.e., accept the thermal cracking and product degradation that occurs as stripper vapors are thermally cracked. Those refiners wanting to improve the situation have had only two options – build a new, separate stripper in a separate vessel or build a "containment vessel" of some sort within the existing reactor/stripper vessel. Each option has problems.

### SEPARATE VESSEL – COST/SPACE CONSTRAINTS

The costs to modify a unit by putting in a new, separate stripper are usually excessive and usually not an option. Most refineries do not have enough space between units to put in a new catalyst stripper. Even if the space were available, the economics are such that it doesn't pay, so most refiners just stay with their existing strippers, rather than put in a new separate stripper.

### CONTAINMENT VESSEL – COST/MECHANICAL CONSTRAINTS

Ross, US 4,946,656 taught a way to quickly get stripper vapors from above an FCC stripper but the "solution" created problems. Complete isolation of a stripper, as in '656, must be done within the constraints of the unit. Cyclone diplegs and risers must be able to pass through any containment vessel, to permit flow of spent catalyst down into the stripper, both from the riser cyclones receiving large catalyst flows discharged from the riser reactor as well as much smaller

flows from secondary cyclone diplegs. Stripper vapors have to be able to flow up through the containment vessel to be removed.

In FCC regenerators, there are tremendous temperature swings, primarily during startup, but also during normal operation and shutdowns. Temperatures go from ambient to 1300 – 1500°F. Diplegs “grow” significantly in length during startup. The equipment is also heavy. The equipment has to be heavy to stand up to years of continuous sand blasting in the FCC unit.

It will be difficult to have a long run length with the device disclosed in ‘656, with a conical element 31 beneath a pipe 30, all of which have to fit through another conical element 40 which forms the “containment vessel”. Because cone 31 is larger than hole 29, building, or at least assembling, the device within the FCC reactor is required. Conical element 31, in isolating the stripper, makes it harder to work on and service the stripper, the baffle plates of which usually require extensive repair during turnarounds every 2 – 3 years. Finally, the fact that pipe 30 has to extend sideways and down creates concerns that support of this pipe will bind in hole 31 or break off.

I have visited, and from contacts in the industry know of, many FCC strippers, but have never seen or heard of a confined stripper, such as that disclosed in ‘656.

Chitnis, et al. US 5,681,450 teaches an improved third stage separator (TSS), a device used to eliminate traces of catalyst fines from flue gas before it is discharged to the atmosphere. The TSS is used in, or rather downstream of, a regenerator. In the regenerator, the first stage, or primary, cyclones recover “more than 99 % of the total solids...” “The secondary FCC regenerator cyclones treat as much gas as the primary cyclones, but orders of magnitude less solids. Secondary cyclones recover typically around 95 – 98 % of the solids...” “Third stage separator cyclone operation is characterized by large volumes of gas and small amounts of extremely fine particulates, much of it smaller than 5 microns.” Col. 6, line 51 through Col. 7, line 3.

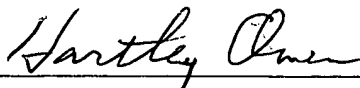
In summary, the Chitnis device is for use in the regenerator, not the reactor. It is for a 3<sup>rd</sup> stage separator, preferably housed in a separate vessel Col. 17, line 39/40. This is remote from a catalyst stripper.

One skilled in the cracking arts would not consider the problems of TSS units similar to those of a catalyst stripper. As one example, the catalyst stripper has tons (literally!) of catalyst with an average particle size of 60 – 80 microns or so and little gas. The TSS unit sees enormous volumes of gas and almost no catalyst. The only solids are fines, typically less than 5 microns diameter. The cracking catalyst particles are over 1000 times larger than the fines captured by TSS units.

Lomas in US 5,584,985 teaches a stripper vessel or “separation vessel” inside another vessel. Like Ross, discussed above, Lomas relies on hardware to isolate the stripper vessel.

In my process, fluid dynamics and a snorkel tube quickly get stripper vapors out, before they can thermally crack and degrade. This can be done at relatively low cost, using a snorkel rather than building a containment vessel for the stripper or a separate vessel to hold the stripper.

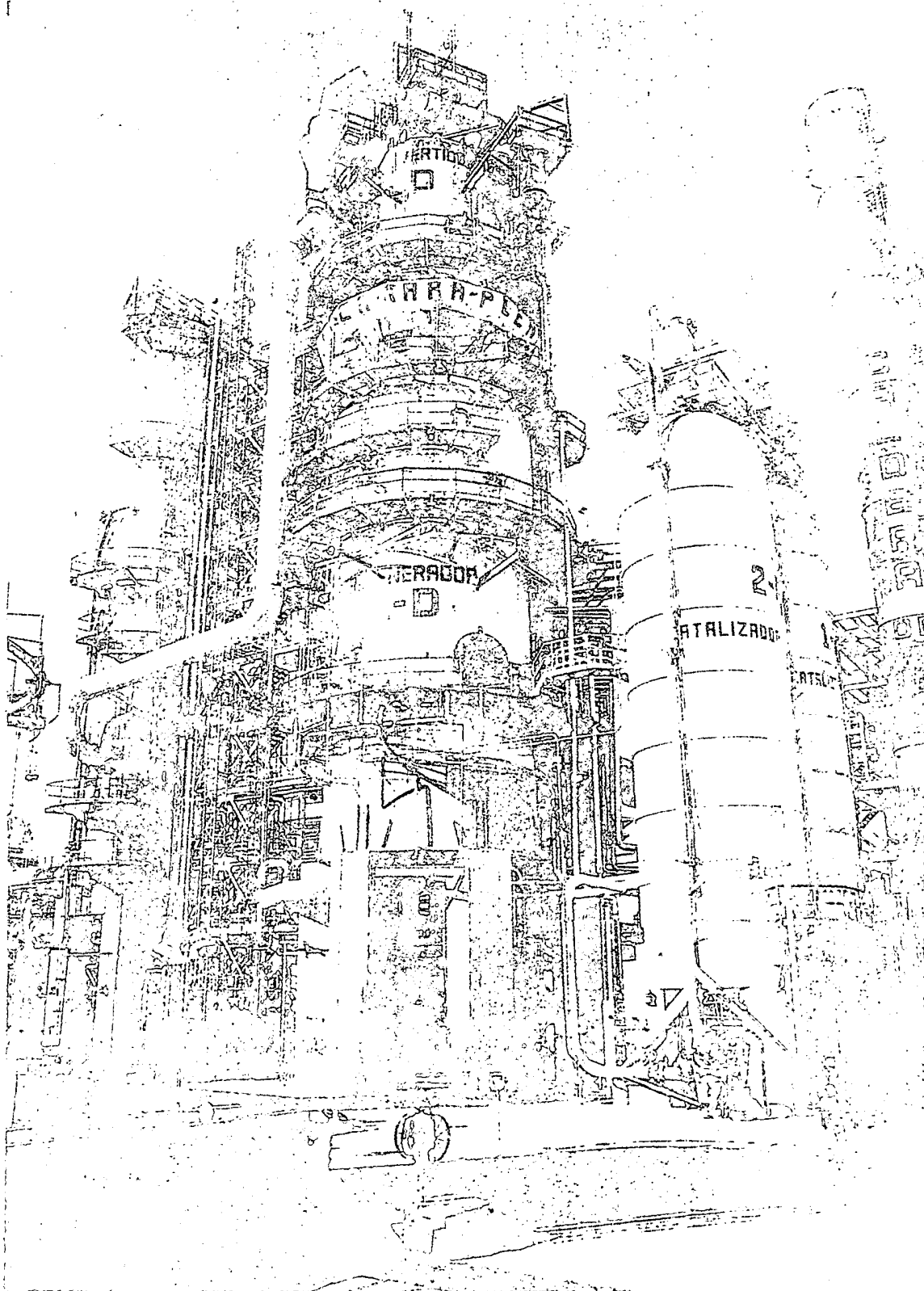
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

  
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Hartley Owen

12-21-06  
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Date

# OIL & GAS JOURNAL

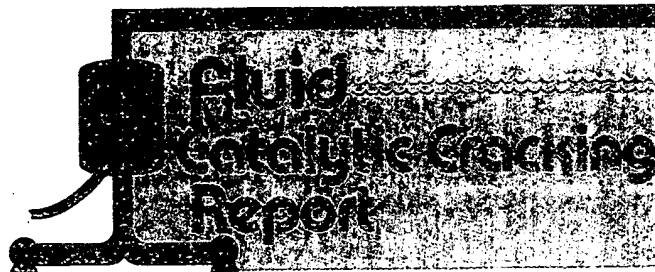
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FLUID  
CATALYTIC  
CRACKING  
PROCESS

SECTION  
OF  
CATALYTIC  
CRACKING  
UNIT  
SHOWING  
CATALYST  
CIRCULATION  
SYSTEM

Continued



## Innovative improvements

### highlight FCC's past and future

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Advances in catalytic cracking led to the invention of a new unit operation—fluidization of fine powders—nearly 50 years ago. Fluid catalytic cracking (FCC) is still the major use of fluidization, and it is the focus of most fluidization research in industry.

FCC owes its longevity, compared to thermal and other catalytic processes, to its remarkable adaptability to changing demands. Far from ever being a mature technology, FCC will have to keep evolving to meet future challenges.

The commercialization of

catalytic cracking in fixed, moving, and fluid-bed reactors offers many lessons in chemical reaction engineering, and maybe more importantly, in the management of technical innovation and in the art of technology transfer from the inventor's mind, through a tortuous path, to steel, concrete, and finished catalyst.

#### Catalytic cracking evolves

The increasing use of the automobile at the beginning of the 20th Century had more widespread impact on the petroleum refining industry than any other modern invention. Fuel needs of the internal combustion engine quickly consumed available natural gasoline, which became the most valuable refined product.

To meet the needs, petroleum companies have been finding and producing more crude oil. But complex supply

and distribution considerations, coupled with recurring energy crises, have always stressed the need for refiners to upgrade less valuable petroleum products to gasoline.

This need spurred William Burton, of crude-poor Standard Oil Co. of Indiana, to commercialize the first thermal cracking process in 1913. Two other methods to upgrade heavy ends to gasoline were developed later: catalytic cracking and hydrocracking (Table 1).

A major inefficiency in these processes is the production of low-value coke. The three process routes have dealt differently with this problem.

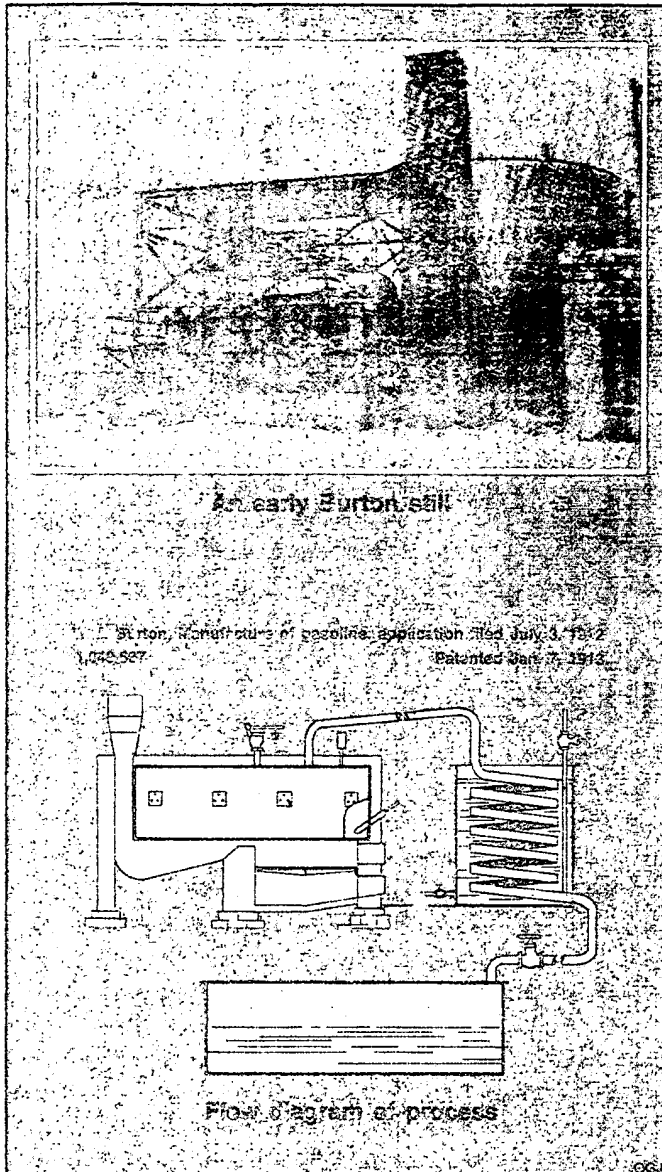
Hydrocracking suppresses coke formation by recirculating hydrogen at high pressure, while Houdry discovered that burning coke restores catalyst activity. Three major chemical reaction engineering solutions have been applied to implementing Hou-

#### 50 years of catalytic cracking

*Fifty years ago, several U.S. oil companies were engaged in research and process development that would shape the industry for years to come.*

*In 1936, the first commercial fixed-bed catalytic cracker had gone on-line. Six years later, the first commercial fluid catalytic cracking unit was on stream. That short period could be characterized as one of the most fruitful ever in oil industry research and development. This major article chronicles the evolution of catalytic cracking, a technology that is still evolving and that will see more advances even beyond the final decade of this century.*

## Burton process was first thermal cracking



## Key dates in cracking technology

Route	First commercialization	Current status
Thermal cracking	Five major processes from 1913 to 1936	Similar processes (coking, visbreaking)
Catalytic cracking	Houdry process, 1936 (following unsuccessful McAfee process, 1915)	FCC is a major refinery upgrading process
Hydrocracking	Many attempts (leading to coal hydrogenation) prior to modern HDC, 1932	HDC complements and competes with FCC

dry's invention: fixed bed (1936-1941), moving bed (1941-1955), and fluid bed (1942-today). The dates in parentheses represent the heydays of each process.

As is common with many other processes, old units usually gradually fade away. It may take a long time to replace an old, reliable, fully depreciated refining unit with a more efficient one.

The advantages of each process offer a unique study in chemical reaction engineering. The fixed bed provides efficient plug-flow contact between gas and solid. Its commercialization by Houdry, Socony-Vacuum, and Sun represents not only persistence of determined inventors, but also a major milestone in process technology.

Houdry process innovations include process control brought about by cyclic operation, synthetic catalysts, and the salt-bath reactor. The moving-bed was a major innovation in continuous opera-

tion, while still maintaining good gas-solids contact.

Yet, despite the complex elegance and profitability of the moving bed, another unit operation emerged as the eventual winner.

Why did a less efficient contactor, the fluid-bed, gain prominence in catalytic cracking? One of our major objectives is to explain the technical, historical and technological management aspects of this story.

Catalytic cracking, as we know and use it today, is mostly performed in a fluid-bed system. However, this was not obvious in the 1940s or early 1950s.

For example, yields and operating costs were similar for FCC and Thermoform catalytic cracking (TCC) with the relatively mild operating conditions of those days.

One important lesson is that selection of a technically superior process offers future flexibility. The managerial vision that was needed at the time transcended simple accepted economic analysis and political considerations.

The advent of FCC introduced a new unit operation—the fluidization of fine powders. FCC is still the major user of fluidization of fine powders, and most industrial research in fluidization is done to support the FCC process.

However, fluidization is only one aspect of catalytic cracking, and we believe it is important for researchers in academia to appreciate other FCC concerns. We will dic-

A BATTERY of Burton-Clark cracking stills, each 2-1/2 ft by 30 ft long, processing a 325 gal batch (Fig. 2).

100-443887-100

For the past 60 years, from the 1920s until the 1980s, the "working man of color" has been his own worst enemy. By not fully embracing the development of the nation's history, the working man of color has been a victim of the economic process.

1. In re: the thermal cracking process patent awarded to Wm. Burton on Jan. 7, 1913. Universal Oil Products Co. owned by E. C. Coker, who as a result of purchasing the Standard Asphalt Co. and the Jesse Jones estate.

1933 A. A. McAfee of Gulf Refining Co. discovered that a Friedel-Crafts aluminum chloride catalyst could be used for isobutylene.

1940's Queens process became popular and widely used.

1940: Eugene Henry turned to research in the  
cancer field.

1999: Houdry process demonstrated positive potential in Europe.

East Western Oil Co. authorized \$100,000 and set up 70 oil demonstration units at Painsboro, N.J.

2025 Release Under E.O. 14176

[illegible]

YOUNG & Rubicam of media. O. Co. discovered  
certain errors of the day, recorded from 1903 on  
the last operators.

1995, Rodery-Vanum Oil Co. (formed in 1981 by merger of Vanum Oil Co. and Standard Oil Co. of New York) agreed to contribute \$5.6 million to Housing Progress, Inc. and its housing development efforts. Idea of making catalyst between reactor and regenerators rather than switching reactors or fixed-bed catalysts.

[illegible]

1. *Chloroceryle alpestris* (C. alpestris) first studied (sexed and aged) in 1966 at the S. J. Estey Wildlife Lab., approximately 100 km. S.E. of Saskatoon (2100' S.W. West-based Canada) during the fall of 1966. P. J.

1. United Arab Emirates - Abu Dhabi, Ajman, Ras Al Khaimah, Sharjah, Umm Al-Qaywayn

of the former a constitution or right of appeal to the  
Spray-to-Research Association for the purpose of re-  
ceiving one-half of the profits of the said business.

1935: 100 cfm unit at Standard Oil Co. operated in powder operation and renamed 250A. Unit made fluidized-bed unit.

1948: Heavy units: processing capacity lifted 140,000 and in 14 plants. Four thermal crackers at Imperial revamped to "suspension crackers" by adding 2-10 lb. powder/bbl. feed. Standard Oil Co. of Ind. appropriated money for first commercial cracking plant. Houdry and Socony-Vacuum built synthetic catalyst plant at Paulsboro.

1941: First 600 b/d semicommercial buckel-olene  
Thermofor catalytic cracking (TCC) unit went on stream  
at Socony Vacuum's Paulsboro refinery.

1942: First commercial FCC unit started up, 1,200  
bbl. PEGC-1 (Model 1) at Standard Oil Co. of Ind.'s  
Baton Rouge, La., refinery. Cities Service installed 3  
FCCU's called the "3 Sisters" at Lake Charles.

1943: first commercial. 10,000 b/c 700 unit with a stream at Midland Oil Co's Beaumont, Tex. plant.

1944: FCC reactor changed to downflow (Model II).

1957: Houdry Process Co. developed the "four-way" process. Socony-Vacuum developed the air-1 FCC process. UOP introduced stacked FCCs with 5,000 bbl./hour unit in Detroit. Improved delayed-product design FCCs (Model III) introduced.

1948: Davison Chemical Co. developed microsphe-  
rical MS-FC catalyst

1950: First air-lift TCC unit starts in stream at Beaumont refinery. Lewis and Gilliland fluid process patent awarded Feb. 21

1951 M.W. Kellogg Co. began offering Chard-Loy design (further down A)

252 Low elevation FCCs (ridge) common

ask: Short-invented shoe, 25 years old. No more shoe repair, just cracking.

1986 Yellow Pages New England  
1986 East Region Guide

Case #365 Kellogg Orthoflow E. introduced

1964. Dawson developed SCV and REV 500 as a

### 3.5.5. Microbially developed shape-selective ZSM-5 zeolites

cuss both technical and non-technical aspects of FCC development.

The adoption of FCC at Mobil Oil Corp., following Mobil's inventions in fixed bed and moving-bed cracking and in zeolite catalysis, will be traced. We included some of

the anecdotes of the story  
along the way.

We hope that aside from being entertained, the reader will appreciate the human side of technological development.

It is really the more important one.

## Cat. cracking's history

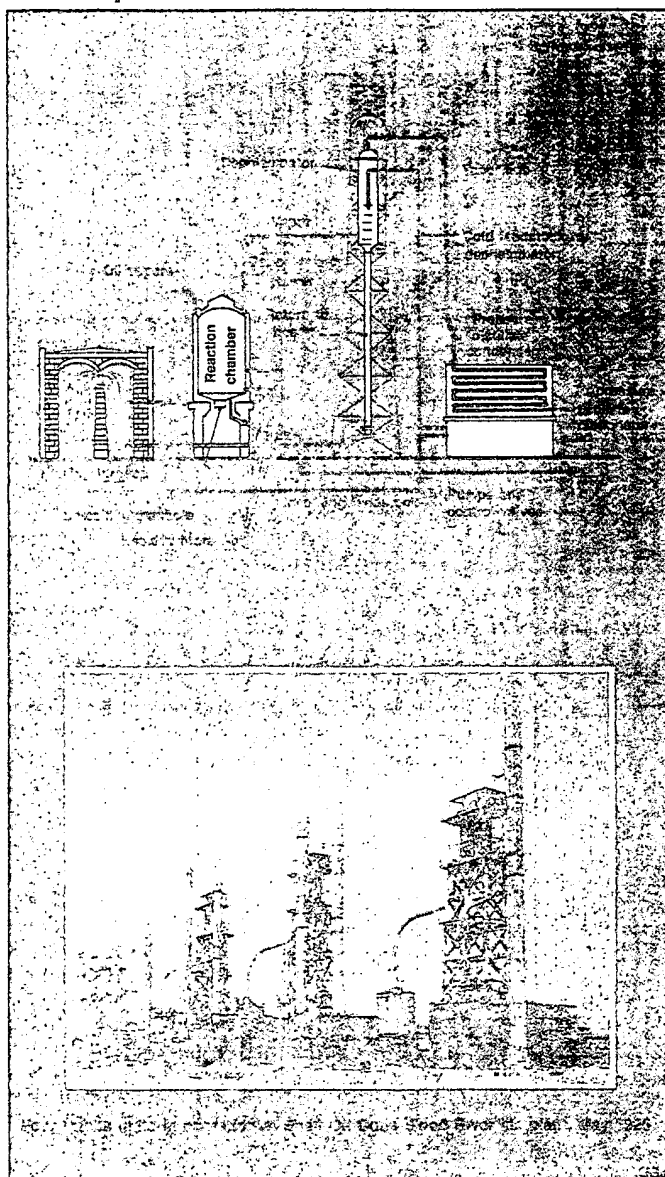
Catalysts were not widely used in petroleum refining until World War II, whereas new catalytic processes for the production of chemicals were being commercialized by the turn of the century.

Research and commercial use of catalysts were particularly strong in Germany. The Haber-Bosch ammonia process (1913), and the synthetic fuels and synthetic rubber efforts of the I. G. Farben cartel in the decades leading to World War II, were notable



Fig. 3

## Dubbs process



highlights.

The requirements of high-octane aviation gasoline as the war expanded finally brought about the wide use of catalytic cracking, polymerization, alkylation, and reforming in petroleum refining.

### First catalyst use

The first commercial trial of catalytic cracking came early in 1915. A. M. McAfee, of Gulf Refining Co. (now Chevron), discovered that aluminum chloride (a Friedel Crafts catalyst known since 1877) could catalytically crack heavy oils.<sup>1</sup>

While gasoline yield could be increased by 20-30%, the high cost of recovering the catalyst prevented the wide use of this process.<sup>2</sup>

Thermal cracking and coking were the heavy oil upgrading processes of choice at this time, and with the increase in gasoline demand, thermal cracking emerged as the leading gasoline process. Several processes were developed following the commercialization of the revolutionary Burton process (Figs. 1 and 2).

These processes, and the impact they had on the industry, are described by Enos.<sup>3</sup>

One of the most popular ones, the Dubbs process, was widely accepted by the petroleum refining industry in the 1920s.

The Dubbs process was licensed by Universal Oil Products Co. (now UOP),

which was founded in 1913 by T. Ogden Armour by purchasing the Standard Asphalt Co. and the Jesse Dubbs patents.<sup>3</sup> Under the leadership of Jesse's son, Carbon Petroleum (C.P.) Dubbs, Dr. Gustav Egloff, "Gasoline Gus," and later, Haensel and Ipatieff, UOP established itself as a leader in petroleum technology.

UOP guaranteed 23% yield of gasoline and a 24-hr cleanout period for the typical 250 b/d Dubbs unit (Fig. 3), and royalty was set at 15¢/bbl of fresh feed. The Standard Oil companies continued the use and development of other cracking processes, such as the earlier Burton and Cross processes.

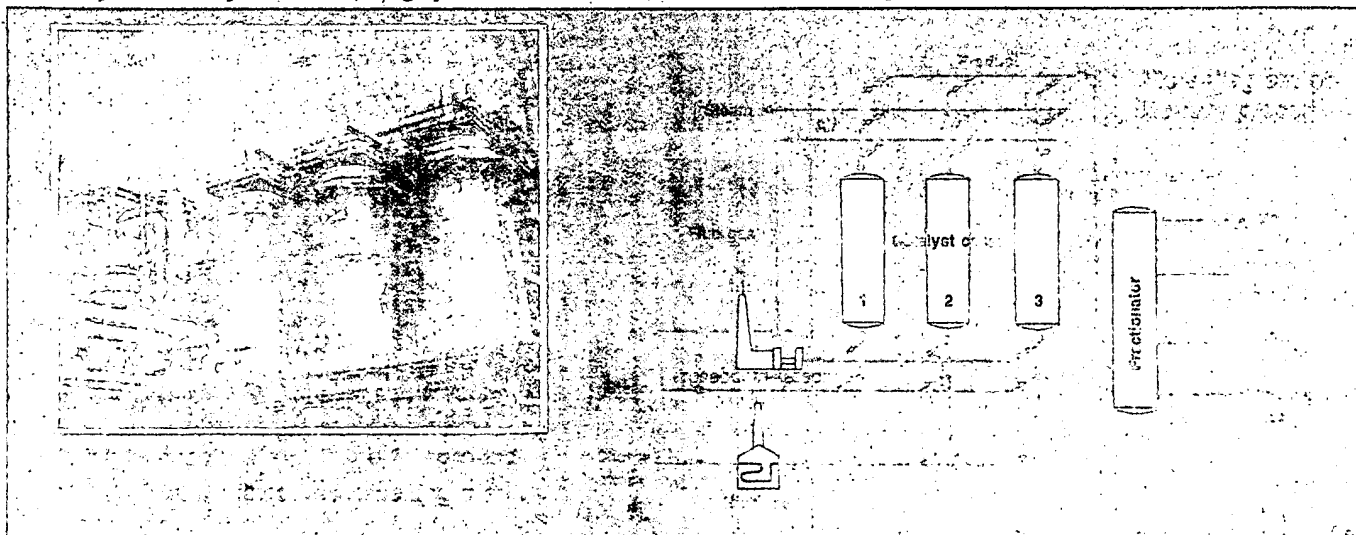
Litigation which followed led Shell and Standard Oil Co. of California (now Chevron Corp.) to purchase UOP in the 1930s.<sup>4</sup>

One of the first hurdles thermally cracked gasoline had to overcome was the color barrier. Unlike water-white natural gasoline, cracked gasoline had a yellowish appearance. Gasoline color was a major quality measure then, and interestingly, it is coming back in the advertising of some gasolines.

It was not until the 1920s that engine performance was tied to a fuel composition. The identification of engine knock caused by premature ignition, the invention of anti-knock compounds, and the octane scale itself, changed

Fig. 4

## Houdry's catalytic cracking process revolutionized refining





It was quickly recognized that thermally cracked gasoline was superior to natural gasoline, and later on, that Houdry's catalytically cracked gasoline was better still.

The invention of catalytic cracking by Houdry, using solid acid catalysts, revolutionized petroleum refining (Fig. 4). Eugene Houdry, a mechanical engineer from a family of steel processors, a star soccer player, a lieutenant in the French Tank Corps in World War I, and an inventor with a unique and colorful personality, started out in petroleum research following the war.

In the 1920s, his major effort, together with French pharmacist E. A. Prud'homme, was converting synthesis gas to liquid hydrocarbons over nickel and cobalt catalysts. While similar efforts in Germany led to the development of the commercial Fischer-Tropsch process, Houdry found no support in France, and in 1927 turned to petroleum conversion.

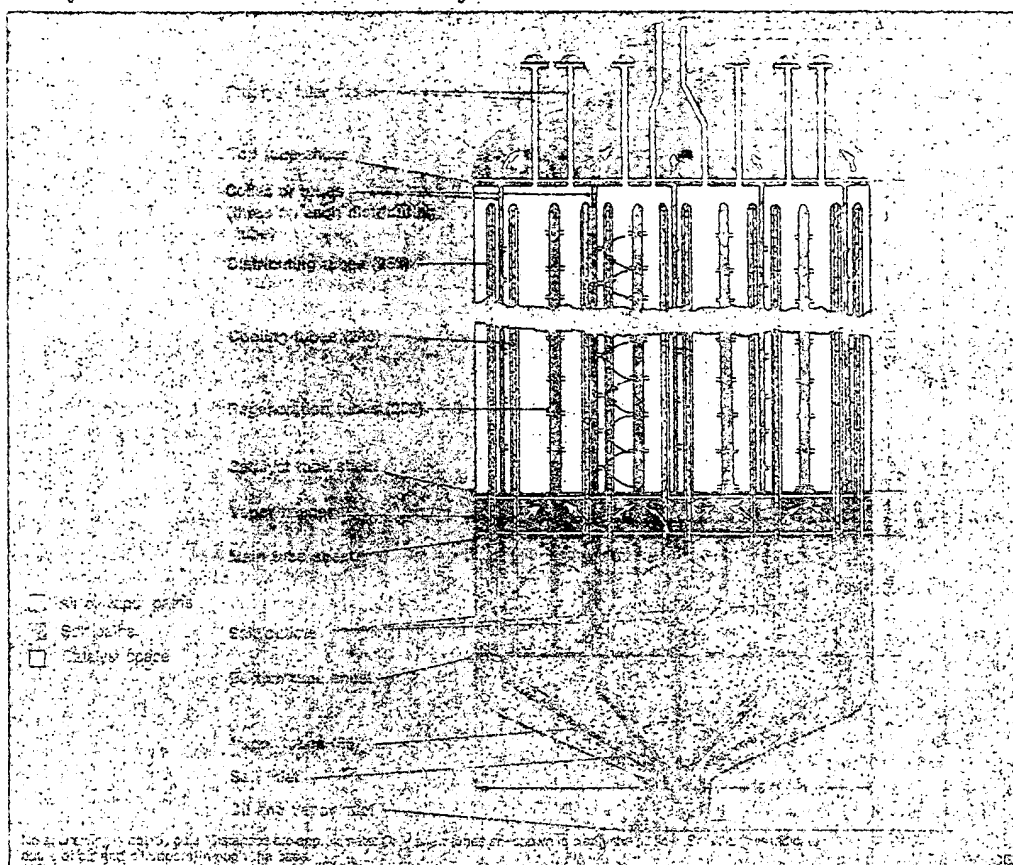
A long-time interest in racing cars had instilled in Houdry the importance of gasoline quality. Silica-alumina catalysts were identified as effective in cracking tar residue to gasoline.

Hundreds of catalyst variations were tried at random and simple tests were used for screening.<sup>5</sup> A tail gas burning with blue or invisible flame indicated uninteresting low molecular weight gas. Color stability and gum formation were checked by hanging bottles of motor fuel on a clothes line in the back of the laboratory.

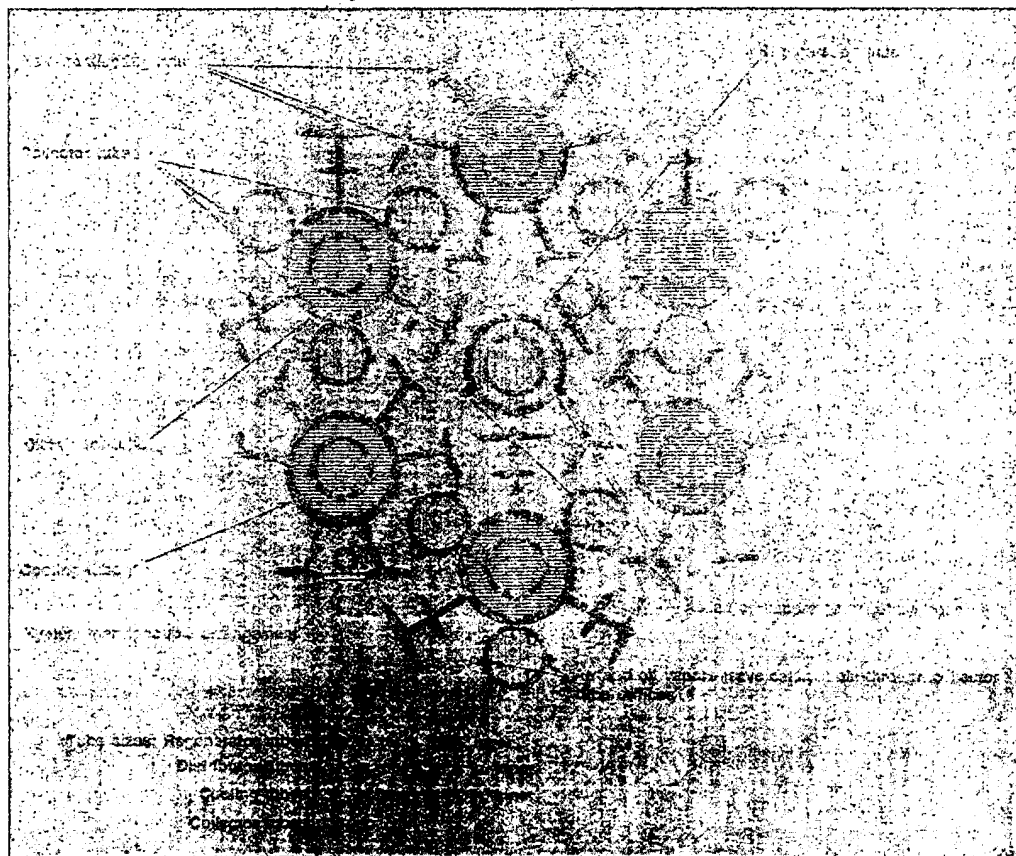
Motor performance was determined in Houdry's Bugatti racing car, by driving up the same calibrated hill. Finally, Houdry settled for an acid-activated clay and established air regeneration to burn coke off the catalyst.

The large oil companies were aware of Houdry's experiments, but most were skeptical. Houdry did interest the Vacuum Oil Co. (later to become Mobil Oil Co.),

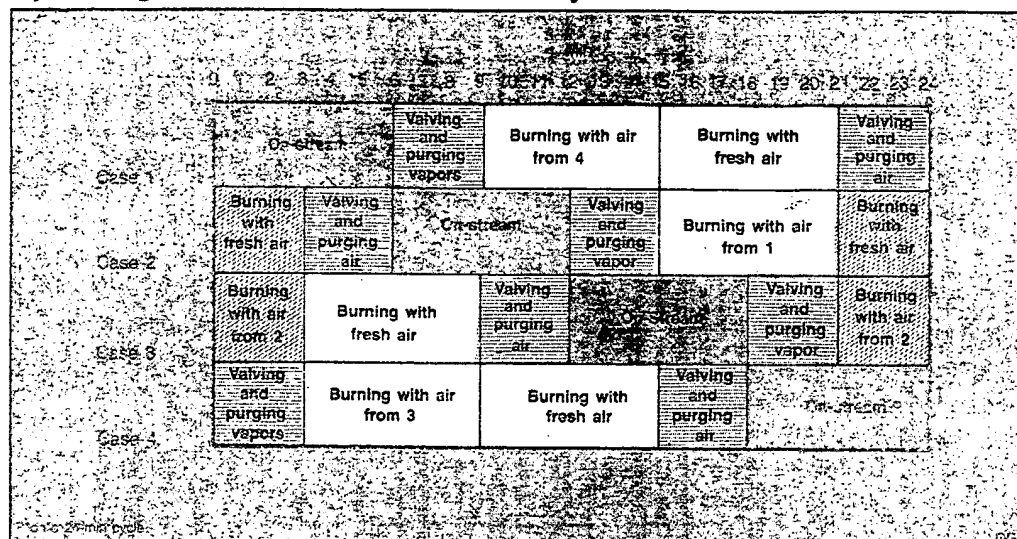
## Simplified commercial Houdry case



Tube section of Houdry case



## Operating modes of four-case Houdry unit\*



whose representatives visited the laboratory at Beauchamps, France, in 1928.

In 1929, Vacuum decided to triple the Paulsboro research laboratory staff from 45 to more than 140, and increase development efforts. Harold Sheets, Vacuum's director in charge of foreign subsidiaries, visited the Houdry laboratory in 1930. His report mentions that, "Results were not up to expectations, but interesting possibilities were seen."

Houdry and Sheets signed

an agreement stipulating that Houdry would come to the U.S. with his apparatus (an 8-in. ID by 14-in. tall catalyst chamber, later called French Unit No. 1 in Mobil's cracking unit designation) and an assistant. Vacuum's board authorized \$100,000 for developing the process if it could be demonstrated for 15 days. When results were positive, Vacuum set up a 70 b/d industrial semi-works at the Paulsboro refinery and in 1931 created, with Houdry, the Houdry Process Co.

(HPC).

Thus started a unique, exciting, and sometimes stormy relationship which led to the successful commercialization of catalytic cracking.

Initial results were positive, but many obstacles had to be overcome. Particularly troublesome were temperature control during regeneration, initially attempted with flue gas recirculation, and complete catalyst regeneration.

HPC funds were running low, and the Great Depression reduced Socony-Vacu-

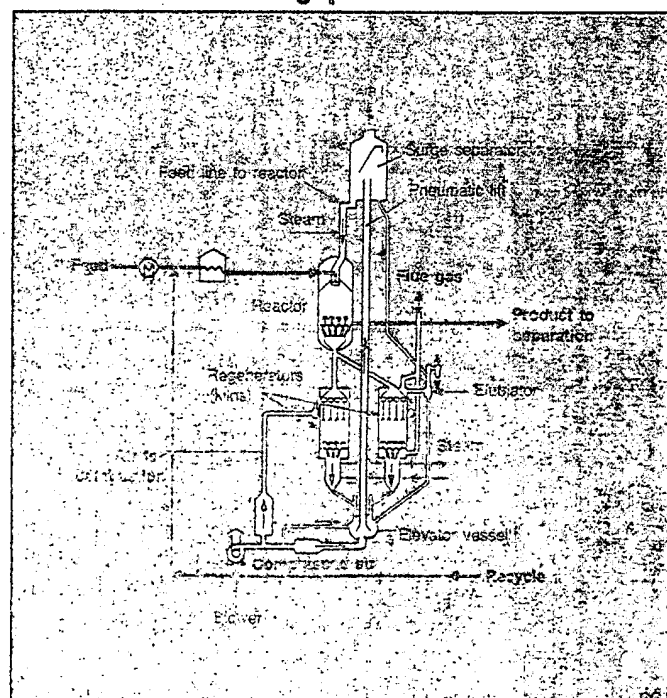
**First commercial unit**

History was made on Apr. 6, 1936, when the first 2,000 b/d commercial cracking unit started up in Paulsboro. This unit, a retrofitted Cross thermal cracker, consisted of three water-cooled reactors. Valve changes required for cyclic operation were made manually.

By the time the process was announced with great fanfare in 1938,<sup>7</sup> two other commercial units were on stream. The first was a 12,000-b/d unit at Sun's Mar-

Fig. 8

## TCC air-lift cracking process



## TCC air-lift reactor design

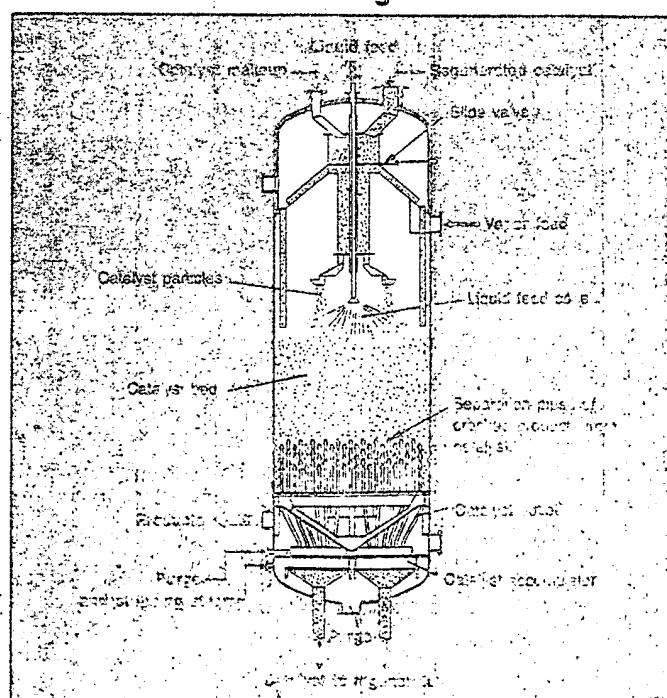


Fig. 9

cus Hook refinery, equipped with motor-operated valves and an automatic cycle timer. Another 3,000-b/d unit was operating at Socony-Vacuum's Naples, Italy, refinery.

At the same time, Socony-Vacuum had eight additional units under construction, representing a \$40 million investment. Licensing to other companies got under way too, and by 1940 there were 14 plants, totalling 140,000 b/d capacity.

Cracked gasoline had excellent front-end volatility and octane, and required a minimum amount of blended alkylate and tetra ethyl lead, to produce 100 octane aviation gasoline. The availability of large volumes of high-quality aviation gasoline to the Allies early in World War II had considerable impact on the war effort.

A simplified schematic drawing of a fixed-bed Houdry "case" (the name comes from French) is shown in Fig. 5. The catalyst occupies the upper two thirds of the vessel, and includes annular tubes for radial distribution of vaporized feed, or air in the regeneration cycle.

Orifices supply the necessary pressure drop for even distribution. Collector tubes with orifices remove the products of cracking or combustion, and molten salt tubes remove the heat of combustion and supply the heat of cracking. A cross-sectional sketch of the tube layout is shown in Fig. 6.

The annular molten salt tubes have cleverly designed fins to assist in heat transfer. The cases were operated in sequence as shown in Fig. 7. The invention of automatic valves and control algorithms revolutionized process engineering.

Even in the perspective of today's technology, the Houdry case was a technological marvel. It took nearly a decade of development by very talented people to invent this elegant breakthrough in process technology.

Yet it was clearly not well-suited for the task. Using large catalyst particles in a fixed bed was common, and the technique of contacting fine powders with gas (in a

## Evolution of a 20,000-b/d FCCU, 1943-1953

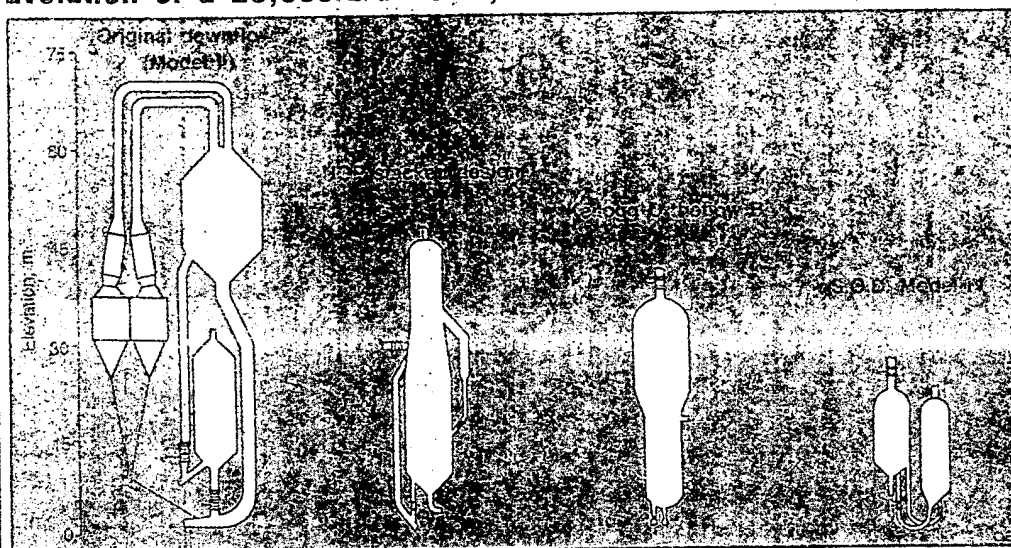
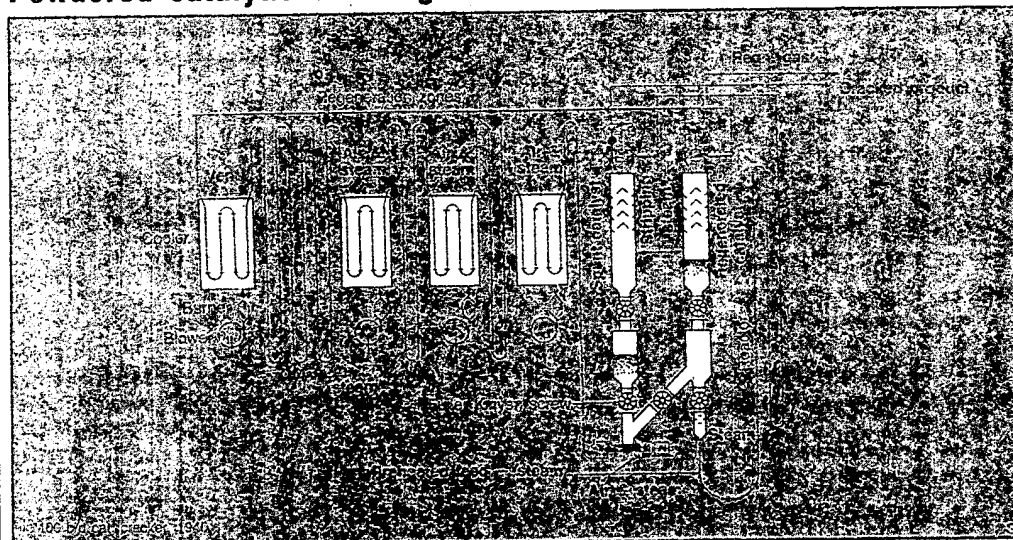


Fig. 11

## Powdered catalytic cracking section\*



fluid bed) had not been invented yet.

The potential to use the Winkler fluid-bed gasifier, recently commercialized at the time for catalytic applications, had gone unnoticed. Small particles should have at least looked attractive because they would increase the rate of diffusion-limited reactions (such as cracking and combustion). The two added benefits of fluid beds, ease of solids circulation, and isothermal operation brought about by solids mixing, were not obvious.

Two innovations were needed to overcome the shortcomings of the fixed bed: a method to circulate the catalyst between reaction

and regeneration zones, and decreasing catalyst particle size. The first innovation resulted in the moving bed, while the combination of the two yielded the fluid-bed reactor of fine powders—a new unit operation with some unexpected benefits and problems.

### Moving-bed cracking

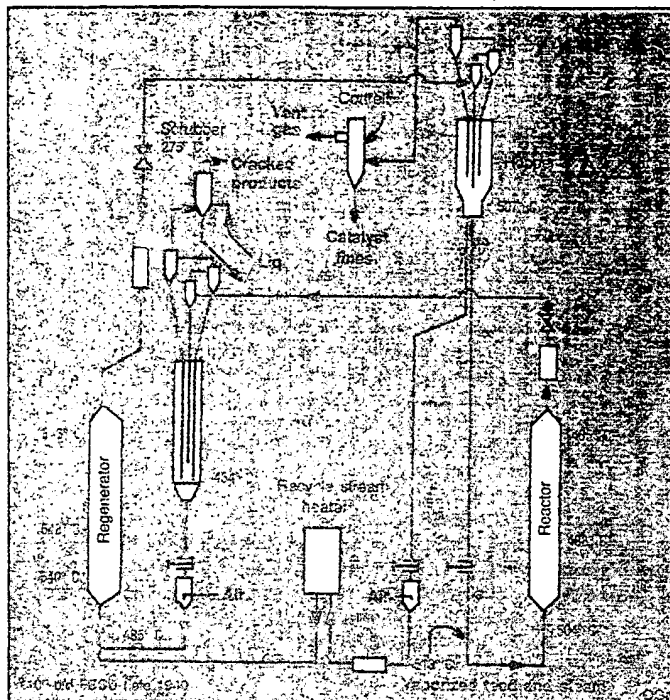
Many technical innovations were quickly implemented after the first fixed-bed catalytic cracker. Socony-Vacuum invented the molten-salt-cooled cracker and, together with HPC, optimized the complex fixed-bed process.

The next step was a continuous cracking process using the Thermoform kiln (which

was used to burn off coke deposited on Fuller's earth in the filtration of lube oils). The first 500 b/d semi-commercial bucket elevator Thermoform Catalytic Cracking (TCC) unit went onstream at the Paulsboro refinery in 1941, and the first 10,000-b/d unit was built by an SV affiliate, Magnolia Oil Co., at its Beaumont, Tex., refinery in 1943. By the end of World War II, TCC capacity was nearly 300,000 b/d.

The important idea of moving cracking catalyst between reaction and regeneration zones, rather than cyclically switching feed and regeneration air, came in 1935. Eventually, the concept was realized in the early bucket ele-

## Hindered settling gravity feed system\*



vator TCC, the Houdrflow, the air-lift TCC, and the fluid catalytic cracking unit.

An early example of such a continuous process was a 500 b/d M.W. Kellogg Co.-designed unit, operated between November 1938 and August 1939 at Anglo-Iranian Oil Co.'s (now BP) Llandarcy, Wales, refinery.<sup>8</sup>

The moving-bed TCC process was being developed separately from the HPC partnership by SV prior to World War II.<sup>9</sup> By 1942, there was an acute war-time demand for high-octane fuels, but the installation of additional Houdry fixed-bed units was not possible.

These units used turbo compressors imported from Switzerland, which could no longer be obtained. HPC reimbursed SV (over \$2 million by 1946) for TCC development, and began licensing the TCC process.

The development of synthetic catalyst beads was a considerable improvement in the TCC process, but TCC still had several disadvantages which made competition with newly developed FCC units difficult following World War II.

Most importantly, the bucket-elevator design was limited in catalyst circulation to a

catalyst/oil weight ratio of approximately 1.5. As a result, TCC was limited to vapor feeds, whereas heavier, partially vaporized feeds were used in FCC.

Both HPC and SV developed improved moving-bed processes following World War II. In 1947, HPC developed the Houdrflow process (after rejecting another solution: an adiabatic, fixed-bed process).

### Air lift developed

At the same time, SV developed the air-lift TCC. Both processes could reach a catalyst-to-oil ratio of 4.

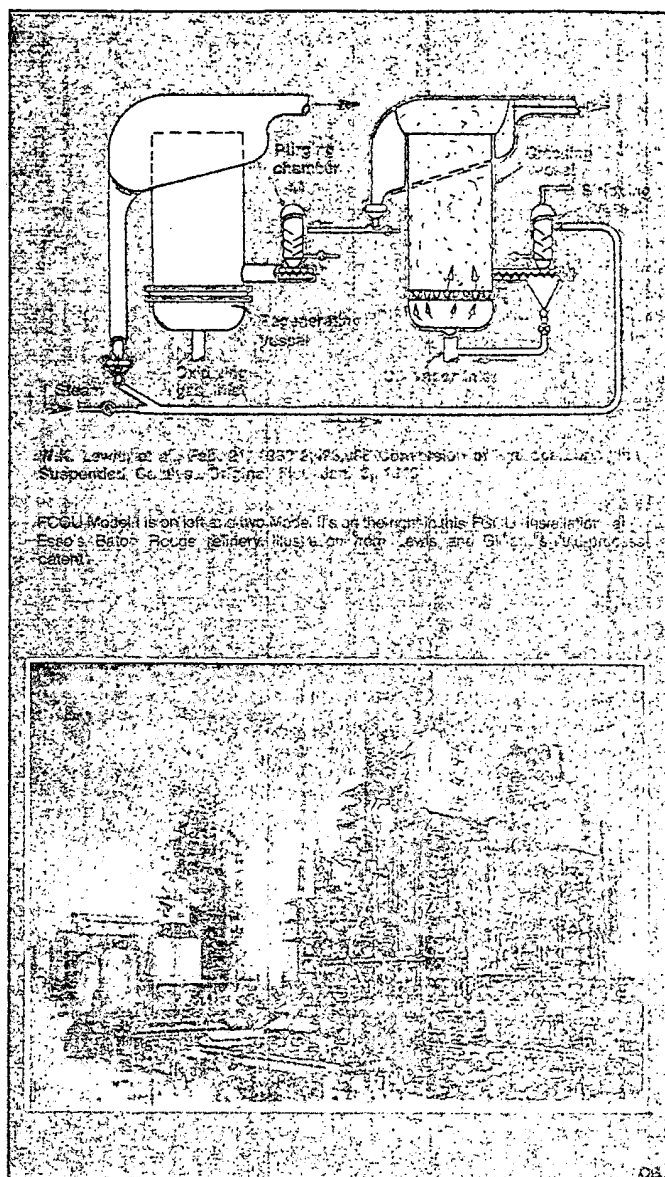
Twenty-one Houdrflow units, with a total capacity of 280,000 b/d, were licensed by 1956. The first air-lift TCC unit came on stream in the Beaumont, Tex., refinery in October 1950, and by 1956 there were 54 SV licensed TCC units.

The moving-bed TCC air-lift process is illustrated in Fig. 8. The reactor vessel is suspended above one or more regenerators (or kilns).

Regenerated catalyst flows out to a lift where it is conveyed pneumatically to a surge separator. The catalyst then flows by gravity to the reactor.

In earlier TCC designs, a

## Model I performance gradually improved



bucket elevator was used in place of the air lift. A simplified schematic of the reactor is shown in Fig. 9.

Catalyst distribution and contact with the feed is carefully accomplished in the upper part of the vessel. Many collector pipes separate the cracked product from the catalyst, and the catalyst is again carefully distributed through a stripper.

TCC units provide excellent contact for steam stripping, and the resulting hydrogen-in-coke levels are as low as 5%, compared with the typical 8% in a good fluid stripper. The stripped catalyst is then burned in an efficient kiln.

Just like the fixed-bed re-

actor before it, the moving-bed system was a marvel of good engineering. It afforded excellent contact between solids and gas in the reactor, stripper, and kiln.

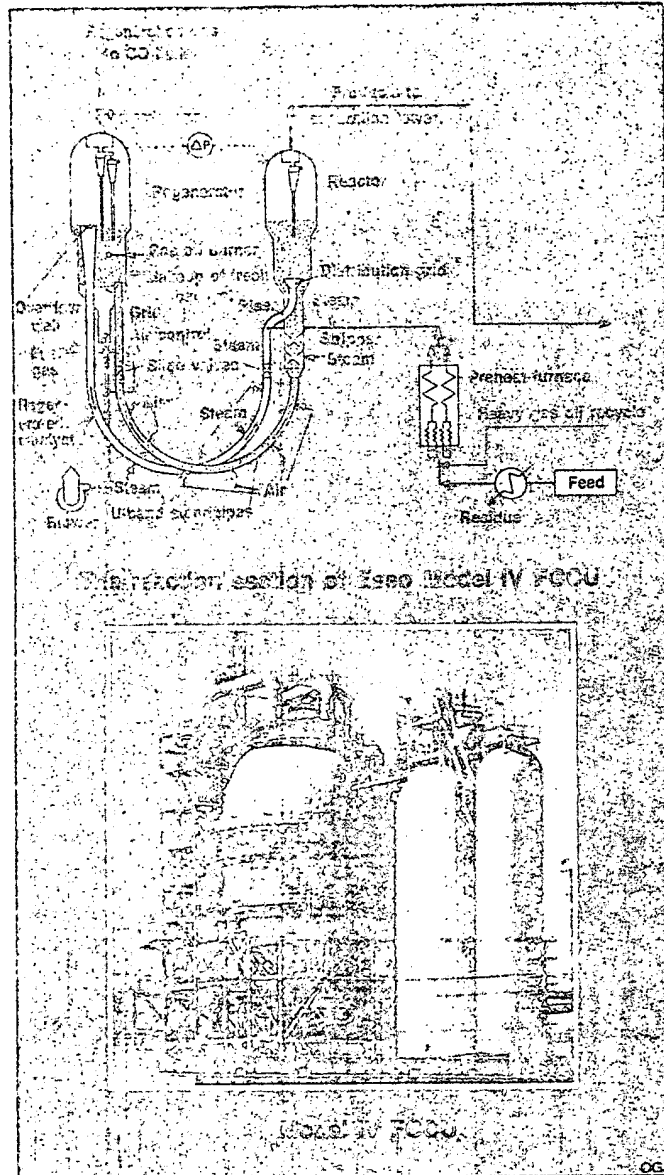
Mechanical details in the design prevented excessive attrition of the bead catalyst in the lift system, and the vessels were filled with carefully designed internals to ensure optimal performance.

The moving bed solved the first problem of cracking elegantly: that of moving the catalyst between efficient contact zones. However, it missed the second chemical reaction engineering principle—the catalyst was still too large.

SV started licensing cata-



## Model IV FCCU



## Shell FCCU designs

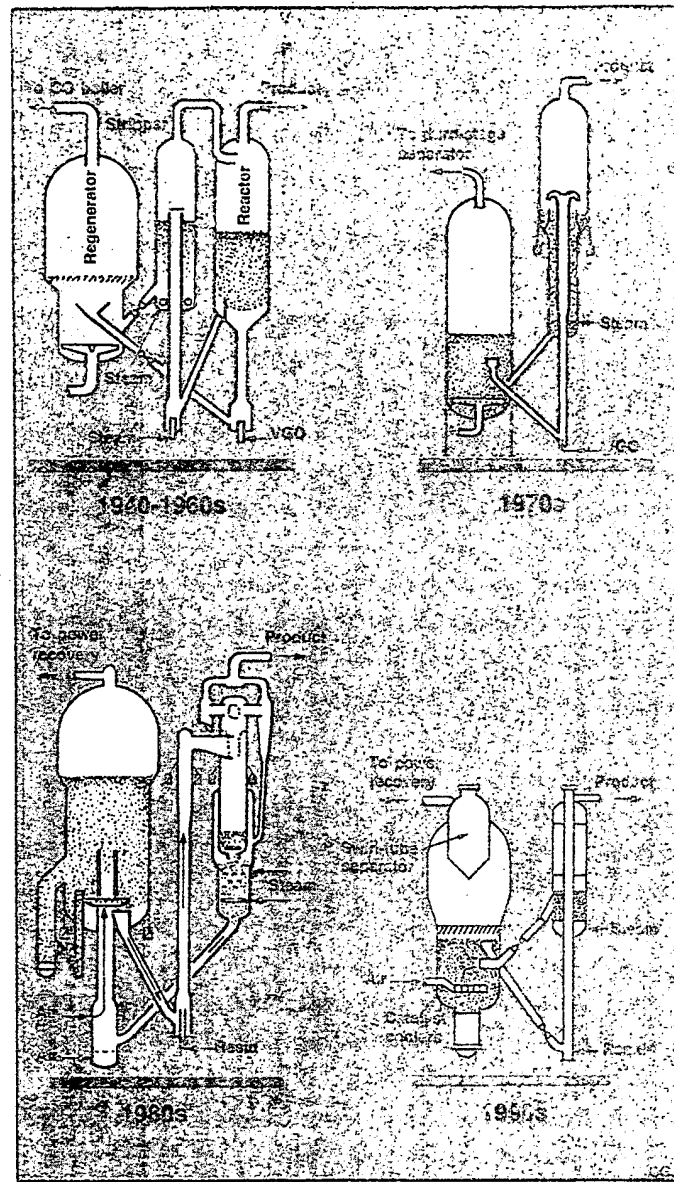


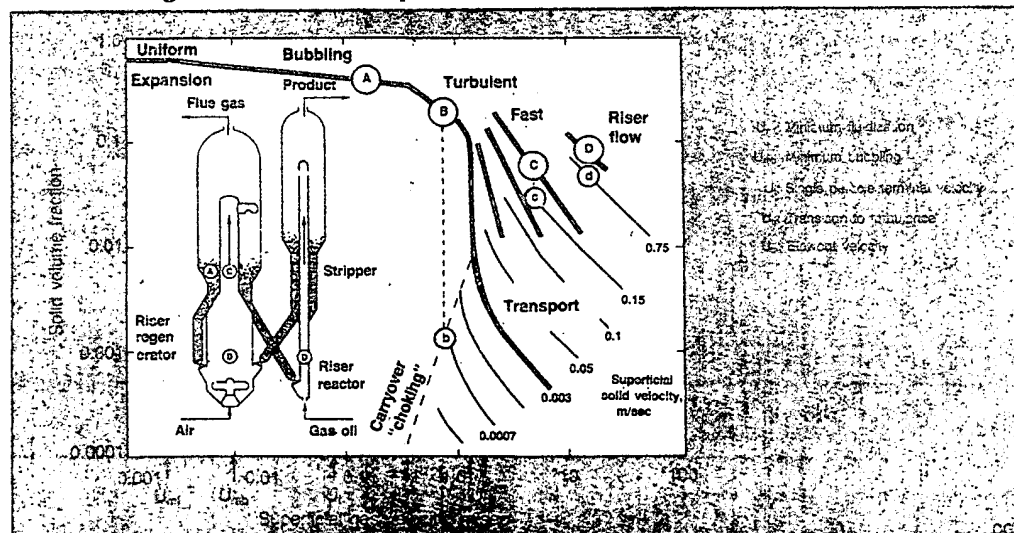
Fig. 16

lytic cracking units by itself in 1949, after finalizing the air-lift TCC design. In a December 1952 memo, Art Danner, SV's head of the process promotion division, summarized SV's cracking activities:

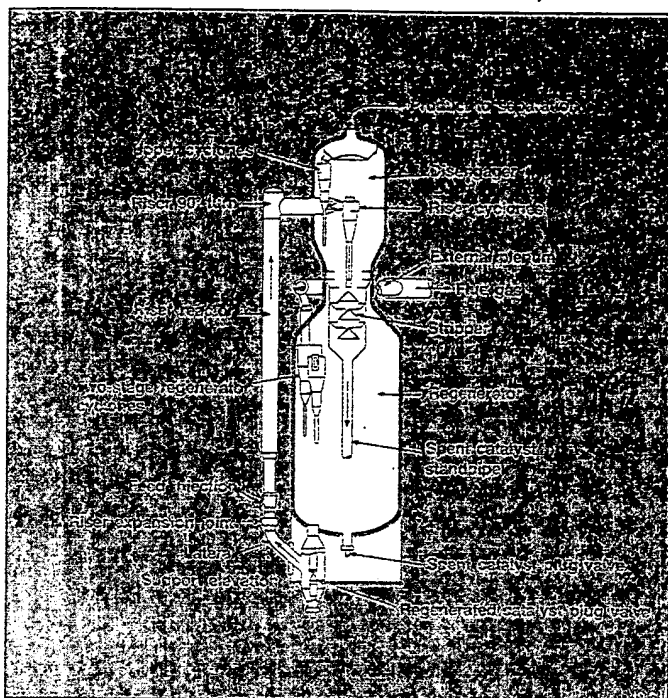
- 1948-1950, initial stage: Designed the new air-lift TCC.
- October 1950-Spring 1952, peak stage: SV enjoyed great success in licensing.
- Current stage: New fluid unit design is better, and SV needs a new design.

Early in the 1950s, the moving bed was competing well with the fluid-bed cracking process. Both processes were similar for light feeds, at the relatively low severity

## Phase diagram of bed expansion for Mobil-UOP FCCU, Group A



# Kellogg's Ultra Orthoflow converter, Model F



cracking and regeneration conditions of those days.

Comparison of the two processes can offer lessons in process development and reactor choice.

Naturally, a technical comparison is only one side of the coin. There are other factors in the licensing of processes which are often the deciding ones.

Houdry's well-known feud with Standard Oil Co. of New Jersey (now Exxon) has been cited as a major factor in the development of FCC.<sup>8</sup> One reason was supposedly the high licensing fee for the Houdry units at \$125/bbl of capacity.

While this was certainly a substantial amount, it was not out of line with other cracking processes, and represented a fair market value. The royalty for the Burton process in 1913 (available only to some refiners, with many restrictions) was 17¢/bbl fresh feed charge.

Houdry's royalty, on the same basis, was 4.1¢/bbl.<sup>9</sup> The royalties charged by Standard Oil of N. J. for the fluid-bed process were the same until Danner lowered the price for air-lift TCC to \$50/bbl of capacity.

The history of petroleum process development in the

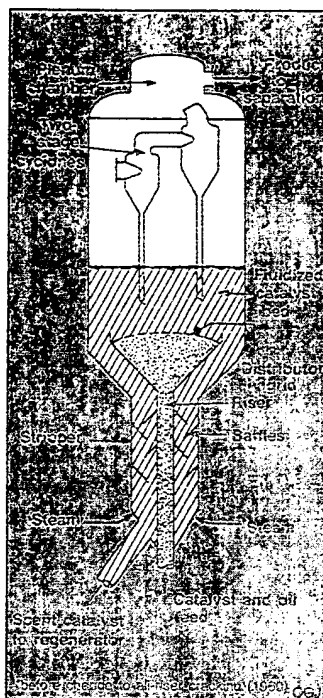
20th century is full of such examples of process innovation, lucrative licensing, development of competitive processes, patent infringement suits, and settlements. This continues to be the case today, and Houdry should not be singled out (as he has been by some) as being a greedy and arrogant soul in an innocent world.

Late in 1952, Danner realized that SV, which was offering the 1949 TCC design, was losing ground to the new fluid processes. SV could not design large (30,000-50,000 b/d) units, or handle larger percentages of liquid feeds.

Fluid-bed units were then being built much more cheaply than moving-bed units, due to lower height (85 ft for the Esso Model IV vs. 270 ft for Model II or TCC, Fig. 10) and were less complex mechanically. The number of licensed TCC's and Houdriflow units declined through the mid-1950s. The Houdry-SV litigation (HPC was suing SV for over \$50 million, and the suit was finally settled for a lower amount) contributed to this decline. Mobil did not start constructing FCC units until the mid-1960s.

**FCC development**  
Fixed-bed catalytic crack-

# UOP's FCCU reactor\*



continues today, and will continue in the future), mutual dislike between Jersey's executives and Houdry, high licensing fees, etc.

In 1934, R. K. Stratford at Jersey's Canadian affiliate (Imperial Oil Co.) discovered that fine clay discarded from lube oil treating had catalytic effects. Four thermal crackers were eventually revamped to "Suspensoid Cracking" by adding 2-10 lb of powder/bbl feed in 1940.

The catalyst was used in a once-through mode, which may be an interesting concept (Chen and Lucki have shown the potential for this concept with zeolite catalysts).<sup>11</sup>

While Jersey decided not to follow this route, development in 1938 switched to a continuous 0.5 b/d pilot plant in which oil vapor conveyed powdered catalysts. Results from the cyclic, fixed-bed 100 b/d pilot plant in Baton Rouge showed that best yields were obtained in the early moments of cracking, underscoring the incentive to develop a continuous cracking process.

It was felt that conveying a fine powder would be easier than conveying pellets. The seeds for the invention of the fluid bed were now planted.

Other highlights in this extraordinary development, which drew upon the talents of over 1,000 professionals in the CRA companies, are shown in Table 2.<sup>10</sup>

The revised 1940 pilot plant (Fig. 11) consisted of a folded reactor riser, still used as an FCC pilot plant at many research laboratories. The spent catalyst stripper was also essentially unchanged, whereas the screw feeder was replaced by standpipes and slide valves.

Standpipes and slide valves provided as good a seal, and provided for better control of solids circulation. Standpipes and slide valves are still used in circulating fluidized systems today.

The late-1940-redesigned 100 b/d FCC pilot plant (Fig. 12) used diameter expansions in the reactor and regenerator vessels to increase solids holdup without use of folded risers. This design

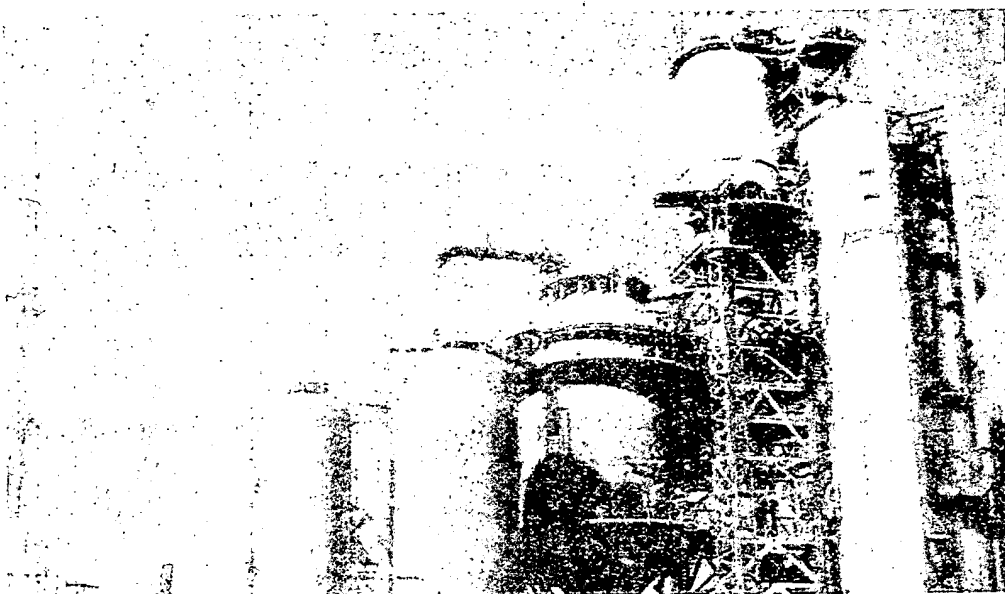
ing was first studied at Standard Oil Co. of N.J.'s (Jersey) Baton Rouge, La., laboratory in 1937.

Initial work with fine powders fed by a screw conveyor was a major development effort.

The use of fine powder, based apparently on a serendipitous discovery by R. K. Stratford in 1934, was the key to the invention of FCC and fluid beds. In 2 years, 400 individuals (one third technical) spent nearly \$1 million on this process.<sup>2</sup>

In 1938, Jersey formed a consortium of eight companies, Jersey, M.W. Kellogg Co., Standard Oil Co. of Indiana, Anglo-Iranian Oil Co., Universal Oil Products Co., The Texas Corp. (now Texaco Inc.), Royal Dutch Shell, and I. G. Farben (which was dropped in 1940), called Catalytic Research Associates, or CRA. CRA's purpose was to develop a catalytic cracking process which would operate outside Houdry's patents.

Various reasons have been cited<sup>8</sup> for this: Standard's reliance on its long-term cooperation with I. G. Farben in hydrocracking (the parallel development of FCC and hydrocracking, and competition between them, con-



GENERAL VIEW of modern side-by-side FCCU with conventional regenerator (Fig. 19).

## Origins of FCC

100 bbl Baron Rouge plant converted to powder operation and renamed "PECLA" Powdered Experimental Catalyst Louisiana.

Table 2

PECLA revised for larger contact time to compensate for low holdup. (Fig. 11)

March 1940

Jersey's board of directors appropriates money for a first commercial cracking plant.

May 9, 1940

PECLA revised to fluid bed, Fuller-Kinoyon pump replaced with standpipe and "star" valve, and later with slide valves. (Fig. 12)

Mid-1940

Start-up of the first commercial FCC unit—15,300 b/d PECLA-1 (Model I) at Jersey's Baron Rouge refinery.

May 25, 1942

cle diameter. This clustering is due to interparticle forces which are as important as hydrodynamic forces for particles smaller than 100  $\mu$ .

For Group C particles (smaller than 30  $\mu$ ), these forces predominate. The high slip velocities in the reactor and regenerator vessels permitted using lower velocities.

### First commercial FCCU

The first commercial FCC Model I was essentially similar to the circulating system shown in Fig. 12. It was the basis for future circulating fluid bed (CFB) systems such as the Synthol reactors, alumina calciners, CFB boilers, and modern FCC units.

The realization that a fixed fluid bed of fine powder will form at gas velocities lower than 1 m/sec, given sufficient disengaging height, led to the development of the Model II FCCU. It was the basis for the turbulent fluid bed concept which is currently used in many catalytic applications of fluidization.

The commercialization of an entirely new unit operation within 5 years was a spectacular achievement. The development of circulating fine powders fluidization apparently had no connection to the technique of using a fixed fluid bed of coarse powders, known since the commercialization of the Winkler gasifier in 1926.<sup>10</sup>

These two fluidization tech-

niques, the American practice of using fine powders and the German practice of using coarse solids, have not yet been successfully merged into a single discipline.<sup>12</sup> While Jersey was aware of the Winkler gasifier, through its joint venture with I. G. Farben, it seems that despite Winkler's later claims, his gasifier did not influence FCC development.

Moreover, Jersey's acquisition of Odell's generic fluid-bed patent,<sup>13</sup> and even the restoration of its disallowed catalytic cracking claims in 1940, was not connected to the development of the American practice.

It is clear from Odell's patent that he was only familiar with coarse solids of Geldart's Groups B and D. For example, his empirical correlation would predict a minimum fluidization velocity of 1 m/sec for a typical FCC catalyst.

Following its successful start-up in May 1942, the first Model I cracker (Fig. 13) performance was gradually improved.<sup>14</sup> By July 1942 its feed rate was already over 17,000 b/d (Table 3).

### FCC becomes high-tech

The capacities of the early FCC units were gradually raised up to three times original capacity through better synthetic catalysts and hardware improvements. During World War II, catalytic crackers were mainly operated to produce high-octane gasoline blending stock, and butylenes for alkylation. Alkylate and gasoline were blended to produce 100 octane aviation gasoline.

After the war, severity was lowered, allowing an increase in throughput. A comparison of the Model I to today's typical FCC unit shows that today's unit yields more gasoline, of higher octane, from a much heavier feed.

### Improvements come rapidly

These improvements were brought about by dramatic developments in catalysts, particularly Mobil's invention of zeolite cracking catalysts in the 1960s, and by improvements in hardware to accom-

## Cracking performance gradually improved

Table 3

	Performance of PECLA-1 on July 23, 1942	Typical high severity 1980s FCC
Reactor feed, b/d	15,000.00	15,000.00
Catalyst/oil weight ratio	3.00	7.00
Weight hourly space velocity	3.00	100.00
Reaction temperature, °C	500.00	545.00
Reactor catalyst rate, tons/min	6.00	13.00
Regenerator temperature, °C	558.00	700.00
Regenerator catalyst rate, tons/min	11.1	14.00
Catalyst losses, tons/day	0.24	0.20
0-20 $\mu$ in catalyst, %	3.00	2.00
Carbon on regenerated catalyst, %	0.44	0.04
Gasoline octane number R+0	82.00	93.50

At a similar feed rate but with a heavier feed, including circulation to a catalyst cooler.

was in part the result of cooperation with Lewis and co-workers at the Massachusetts Institute of Technology.

It was realized that fine powders exhibit a terminal settling velocity far in excess of what the Stokes law would predict based on single parti-



## Zeolite catalysts spurred FCC progress

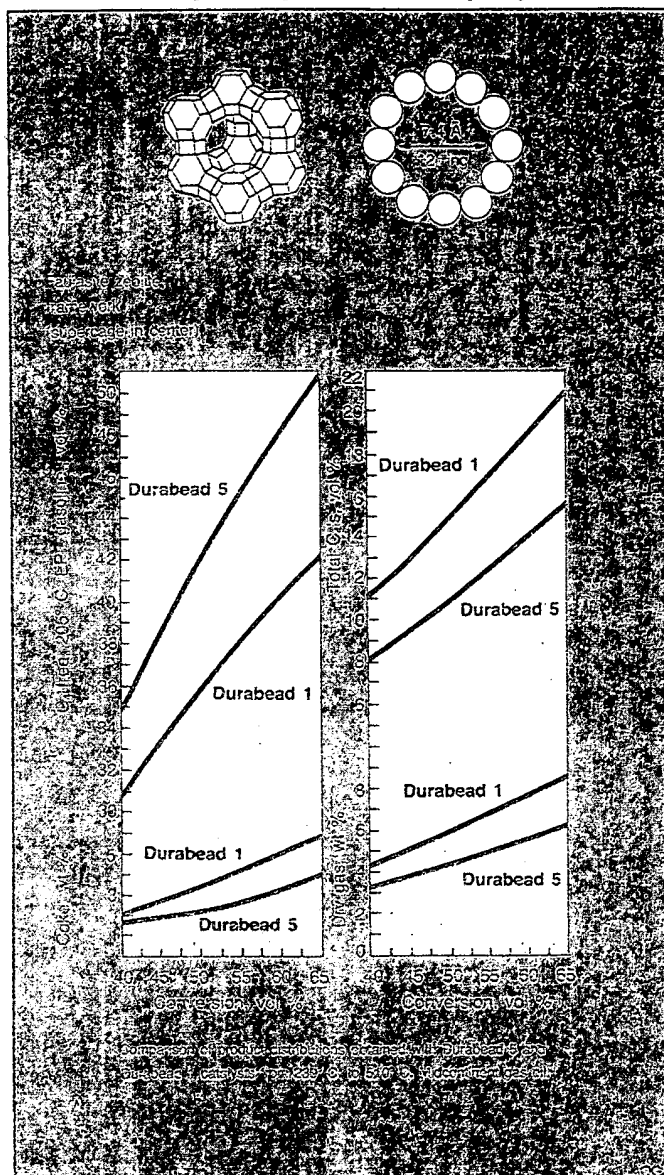
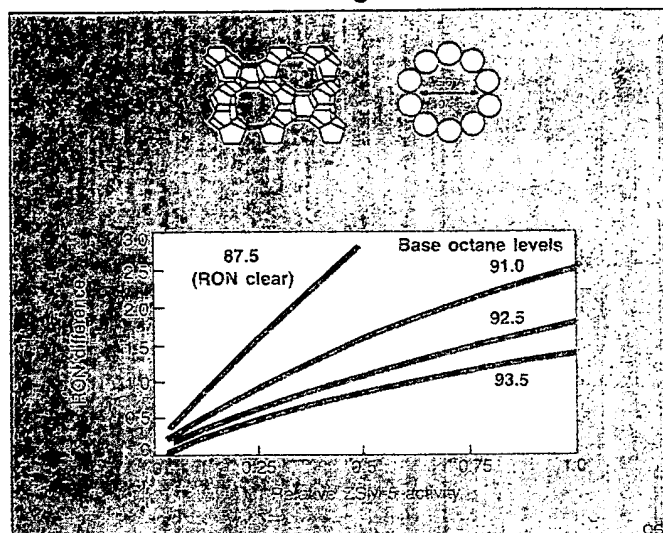


Table 4

### Evolution of FCC features

Model I feature	Later models	Current interest
Catalyst coolers	Developed "heat balanced" concept. All heat produced in regenerator goes to cracking.	To utilize much heavier feeds; catalyst coolers are added to regenerator.
Upflow regenerator and catalyst circulation	To lower regenerator pressure drop, bed height was minimized in downflow.	Mobil-UOP high efficiency regenerator; Amoco's regenerator.
Upflow reactor	Changed to downflow (Model II) to lower overall height and reduce cyclone loading.	All current units have upflow risers; better performance in upflow with higher velocity.
Quick separation	Large volume in reactor freeboard has increased thermal cracking.	Return to various quick separation schemes.
Flue gas precipitator	Cyclones only with downflow and MS catalyst.	Environmental concerns force better dust removal.

## ZSM-5 increases FCC gasoline octane



moderate heavier feeds and take advantage of zeolite catalysts.

Better metallurgy has allowed operation at higher reactor and regenerator temperatures. More coke-selective catalysts have increased the catalyst-to-oil ratio, while the weight hourly space velocity (WHSV) has increased by a factor of 10. Today's FCC reactor is a high-velocity riser with oil and catalyst residence times of only a few seconds.

The Model I unit had several limitations which are obvious in light of the technology that was available, in the 1940s. However, it also had several features which seem very advanced even today.

Some of these were dropped in subsequent models, but are being resurrected. As in many technological developments, some inventions are cyclic and are "reinvented," sometimes by technologists who are unfamiliar with the past—an excellent reason to increase interest in the history of technology. These features are listed in Table 4.

The 1944 Model II, which was being developed as the first three Model I units started up, did offer advantages in the perspective of the times. An improved pressure balanced design, the Model III, emerged after the war.

One of the most enduring and successful designs, the "DC-3" of FCC, was the low-

elevation Model IV design commercialized in 1952 (Fig. 14).

Shell Oil Co. contributed in several ways to FCC development. One of its early Model III units was the first to use microspheroidal (MS) catalyst.

Use of low-attribution MS catalyst permitted elimination of Cottrell precipitation.<sup>2</sup> This also enabled the elimination of waste-heat boilers, which at the time had maintenance problems.

One of Shell's innovations was the Anacortes unit, completed in 1956. It is said to have incorporated many principles derived from TCC.

### Riser cracking debuts

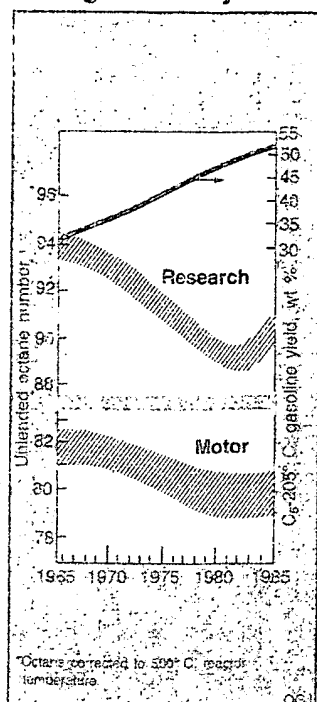
Shell invented the short-residence time FCC riser reactor in two-stage fluid cracking (riser followed by fractionation and a second-stage conventional dense-bed cracker) almost a decade before the widespread use of zeolite fluid cracking catalysts.

The commercial unit was based on several years of process development which considered all aspects of fluid cracking (pilot plants, semi-commercial units, stripping, regeneration, tracer studies, etc.).<sup>15</sup>

The riser reactor was designed to lower overcracking by reducing contact time to as low as 2 sec. While the idea for the Shell riser reactor was possibly based on the

Fig. 22

## FCC gasoline yield \*



original Model I, upflow reactor, short residence time, high temperature, and other concepts were clearly ahead of their time in the Shell system.

Other Shell FCC developments include pioneering use of expander turbines for power recovery, catalyst fines recycle for particle size distribution control, FCC advanced control, and stripper cyclones. The recovery of fines lowers catalyst losses and emission and greatly improves fluidization characteristics.

This is another observation known since the early days of FCC, but it has not yet been fully explained, nor even utilized, by all FCC operators. An FCC catalyst with at least 20% of less than 40  $\mu$  fines can have twice as long a deaeration time as a fines-poor powder.

While judicious standpipe aeration can correct some problems, it can often aggravate the situation and limit catalyst circulation.<sup>16</sup> The use of fines has also been shown effective in reducing bubble size, which would improve shallow-bed regenerator efficiency. Recent Shell efforts have also included residuum cracking as shown in Fig. 15.<sup>17</sup>

## FIA analysis of gasoline fractions

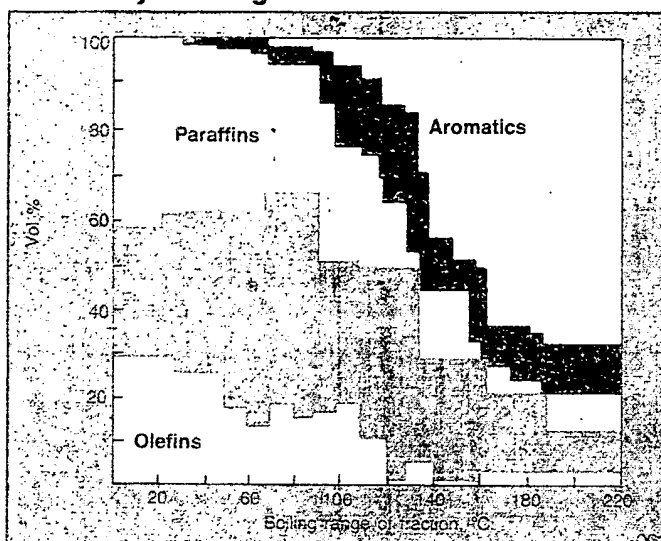


Fig. 23

## Other designs

Other CRA members continued developing their own versions of FCC technology following World War II. After licensing and building the early models, UOP introduced its highly popular stacked unit in 1947 with the 3,000 b/d Aurora unit in Detroit (as in other early FCC units, capacity was increased; to 10,000 b/d in 1953).

Thirty stacked UOP units, typically in the 4,000-10,000 b/d range, were sold mostly to independent refiners in the early 1950s. UOP later built large side-by-side riser FCC units, and together with Mobil, developed the high-efficiency riser regenerator (Fig. 16).

Fig. 16 shows a quantified phase-diagram for fine powder fluidization.<sup>12</sup> Bed solids fraction decreases as gas velocity is increased.

The various fluidization regimes are marked by letters on the phase diagram and on the FCC schematic. It is interesting to note that the Mobil-UOP high-efficiency FCC unit contained all major fluidization regimes.

After the onset of fluidization, the bed goes through a bubbling regime.

This low-velocity regime is used mostly in aerated hoppers, some standpipes, and in most small-scale fluid bed units.

Despite its relatively low significance commercially,

the bubbling regime has attracted considerable attention in academia. The more useful high velocity regimes include turbulent fluidization, which still contains a fixed fluid bed, and the circulating fluid-bed regimes of fast fluidization and pneumatic transport.

Riser flow is a dense conveying regime. The diagram indicates the existence of axial density profiles by using capital letters to denote the density at the bottom of the bed, and lower case letters to denote top density.

In addition, strong and often irregular radial profiles exist, particularly in riser flow. Other highlights of UOP's FCC technology include reliable catalyst coolers and lift gas technology.

M.W. Kellogg designed 47 side-by-side FCC units from 1944 to 1955. These units range in capacity from 4,000 to 60,000 b/d.

In 1951, Kellogg began offering its Orthoflow design (Orthoflow "A") with the reaction and regeneration zones superposed within a single vessel. (Those familiar with the efforts of side-by-side FCC unit operators to avoid intermingling of fuel and air streams can appreciate the courage of "A" operators and the convictions of its designers, where the streams are separated by a thin metal wall and fluid dynamics.)

Vertical catalyst standpipes employed plug valves

to control flow. Six "A" units were built until the introduction of the "B" model in 1958. Regenerator and reactor relative positions were switched. The regenerator was placed above the reactor in the "B" configuration.

Fifteen "B" units were built until the introduction of Orthoflow "C" in the late 1960s, following widespread use of zeolite cracking catalysts. Kellogg, like other FCC vendors, switched to riser cracking to take advantage of those high-activity, coke-selective catalysts.

Ten "C" units were built until the introduction of the "F" units in 1977.<sup>18</sup> Orthoflow "F" (Fig. 17) was the result of evolutionary FCC development efforts at Kellogg. It also includes the "Ultra Cat Regeneration" technology developed by Amoco.<sup>19</sup>

## Mobil's FCC efforts

The last air-lift TCC unit was built in 1960, but the choice between FCC and TCC was not settled by the time Mobil decided to modernize its Torrance, Calif., refinery. This refinery had two bucket TCC units of World War II vintage with a combined capacity of 25,000 b/d of essentially vapor feed.

The TCC design was not competitive in the 1960s, even with Mobil's revolutionary zeolite catalyst, D-5, which was first used commercially at Torrance.<sup>40</sup> Available TCC technology was basically the 1949 design referred to earlier.

It had a pressure drop of 25 psi between the reactor and the atmospheric regenerator. Catalyst was circulated from the regenerator (kiln) to a lift pot above the reactor which was at atmospheric pressure.

The circulation rate was a function of the lift pressure drop, which was limited by the difference in elevation between the bottom of the kiln and the lift pot.

Because the catalytic cracking capacity needed for Torrance was 44,000 b/d, large, twin TCC units would have been required. The heavy feed from Southern California crudes increased the liquid feed capability re-

## Octane drops with boiling point increase

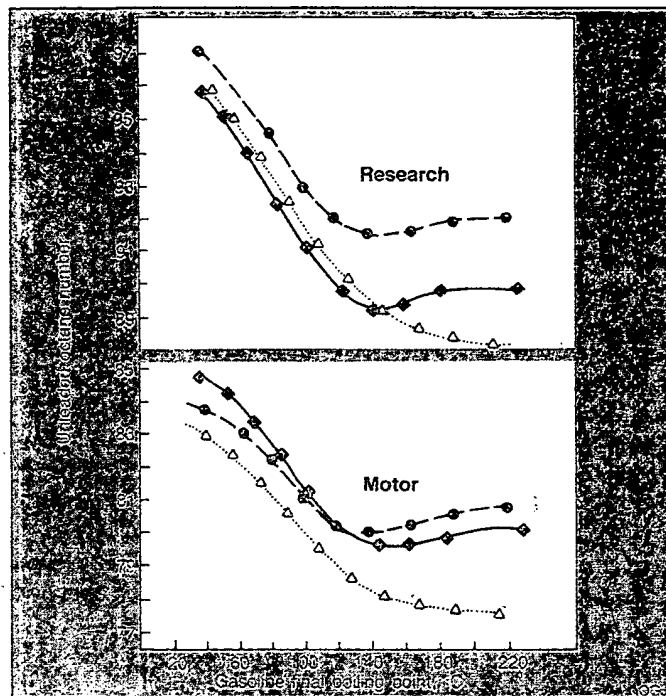
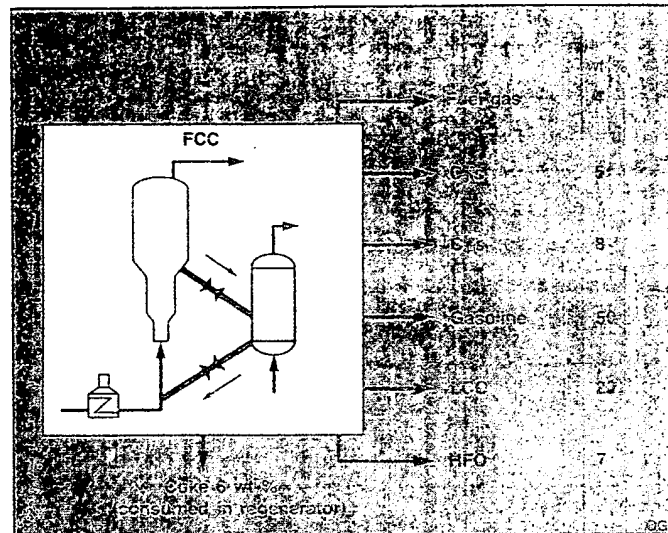


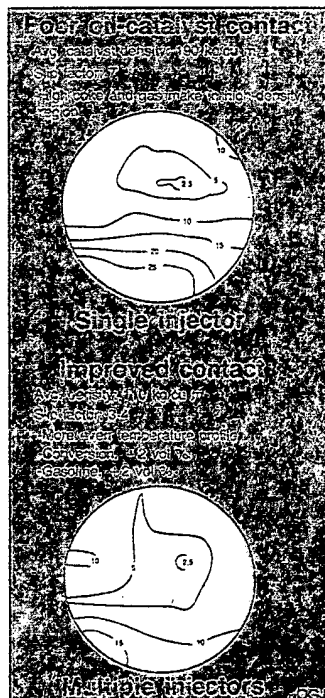
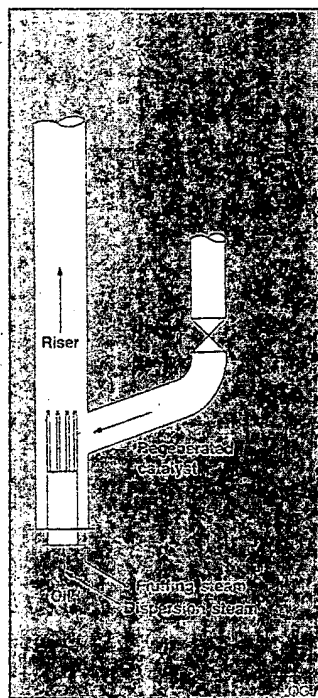
Fig. 26

Fig. 27

## Typical FCC yields



## Multinozzle injection Oil catalyst feed



quirement. An in-house FCC design that won the day was one outlined by the Mobil engineering department in New York.

The closest comparable unit available from a licensor was the UOP side-by-side design with a dense-bed reactor (Fig. 18). A study showed that even with royalty

costs, a 1960 FCC design was cheaper than the TCC design by 20%.

Mobil's engineering department contacted UOP for a proposal. The UOP offering showed that FCC, operating with high activity amorphous catalyst, could match the TCC yield predictions with zeolite catalyst, with the unit

cost advantage intact.

The Torrance FCCU came on stream in 1967, with a new light cycle oil hydro-cracker complementing it from a conversion point of view. The FCCU converted material below 600° C. to gasoline, with a 95 clear research octane. State-of-the-art FCC was now established at Mobil (Fig. 19).

A heavier than design, high nitrogen Southern California feedstock was cracked in the newly constructed FCC unit at 56 vol % conversion (design was 63 vol %). Parallel runs in a TCC pilot plant resulted in only 44 vol % conversion.

The higher density and basic nitrogen content of the actual feed at Torrance had a much greater impact on the diffusion-limited bead than on FCC catalyst. Diffusion is proportional to the square of particle diameter, and TCC beads are 50 times larger than FCC catalyst.

One advantage of a moving bed reactor is plug flow of gas. A moving-bed unit does not require solids control via slide valves, and with a light feed low in contaminants is a viable technology. The disadvantages of TCC in catalytic cracking (and the advantages of a fluidized solids system) are:

- High coke make and feed contaminants can increase reactant and product diffusivity in the larger catalyst particle. The TCC catalyst is ai-

Table 5

## Small particles promote combustion

Temp. °C.	Relative burning rate	
	FCC	TCC
700	340	2.8
650	160	2.8
600	43	2.5
540	11	1.8
480	2.3	1.1
425	0.4	0.4

ways diffusion limited.

- Catalyst beads can turn to "popcorn" or to "rocks" at high temperatures due to excessive internal temperatures.

- It is harder to circulate the larger TCC catalyst. Maximum TCC circulation is one third of FCC for the same pipe diameter.

In TCC, the feed is mostly vaporized to limit coke make, lower catalyst circulation requirements, and decrease feed distribution complexity. The amount of coke burning required in a commercial-size cat cracker is large, approximately 5% of the feed. Ease of combustion with small particles is especially evident at high temperatures (Table 5).

Some of the advantage of the fluid bed is offset in commercial FCC regenerators by backmixing, poor air distribution, etc. Despite this, the superior overall efficiency of the fluid bed system is shown in required unit inventories (Ta-

ble 6).

There were many colorful aspects to the story of FCC development at Mobil. One of the important quality features of an FCC gasoline is its high front-end octane. Mobil sought to demonstrate this by testing commercial FCC gasoline samples.

Two thousand gallons were required for a fleet test, and trucking arrangements were made from a Kentucky refinery to the New Jersey laboratories. At the last moment, the trucker greatly increased the proposed shipping cost and two Mobil engineers ended up in a rented truck driving a load of gasoline over the Allegheny Mountains in a blizzard to successfully complete the mission.

Later, an FCC unit was shown to be economic for Mobil's Beaumont, Tex., refinery to replace two bucket-elevator TCC units. The justified feed rate was 55,000 b/d, and a proposal to duplicate an FCCU that was being built in Mobil's Joliet, Ill., refinery at Beaumont was accepted by the board of directors (rather than design a new unit).

Two years after start-up, the new FCC shut down all five TCC units in Beaumont. It has recently been operating at over 100,000 b/d feed rate.

Soon after building the first grassroots FCC in Torrance, Calif., Mobil embarked on a concerted effort to improve FCC to better utilize high activity zeolites. The new FCC design objectives included:

- Doubling catalyst activity
- Much higher regenerator temperatures (750° C. vs. 675° C.)
- Higher reactor temperatures (over 540° C. vs. 500° C.)
- Much lower reaction contact time (1-8 sec)
- Much lower unit inventory (to 3 tons/1,000 bbl from more than 7)
- Clean burned catalyst (less than 0.1 wt % carbon on clean catalyst vs. 0.3)
- Higher end-point gas oil feed (600° C. vs. 540° C.).

The catalyst was to be a Y-zeolite catalyst developed by Mobil and commercially test-

## Various approaches to feed atomization

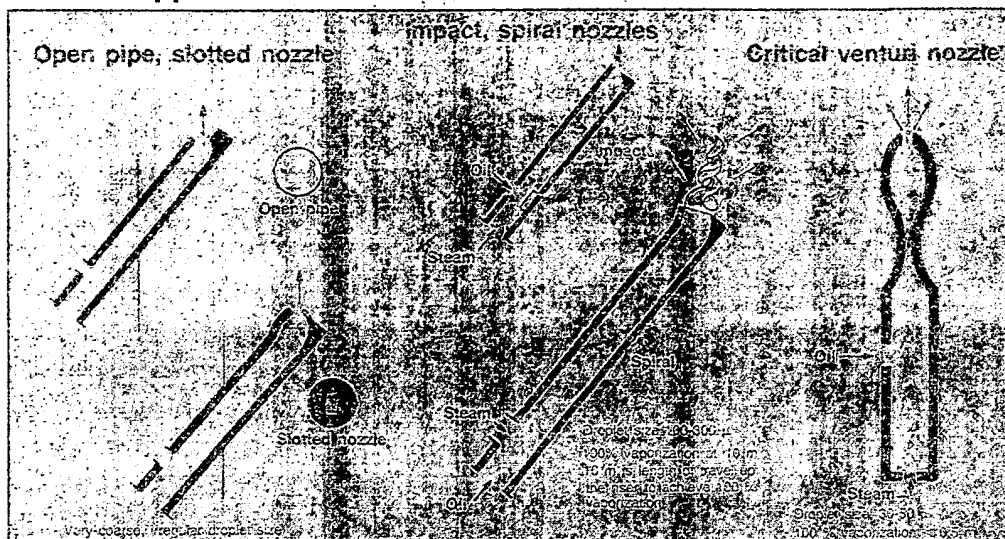
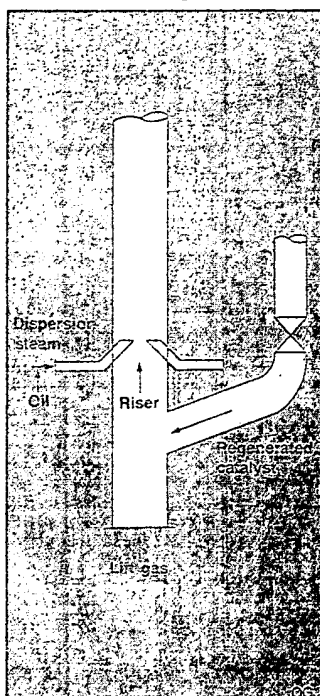


Fig. 29

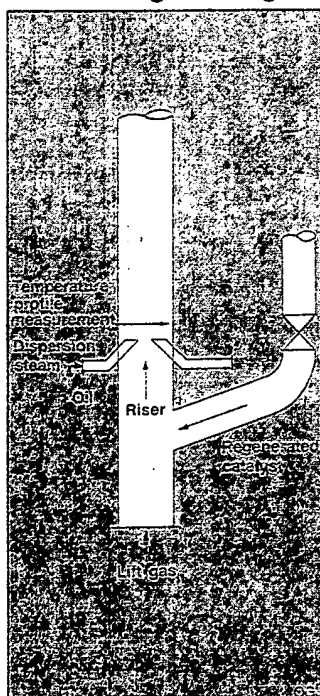
Fig. 30

Fig. 31

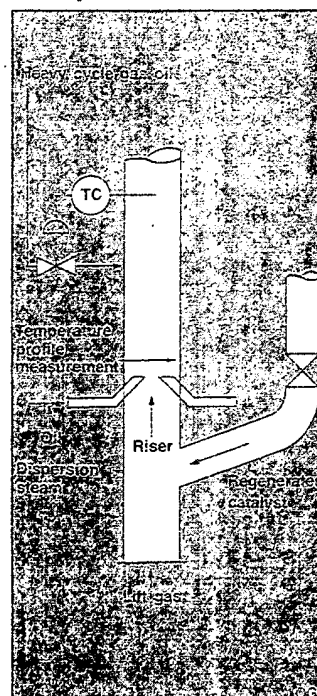
## Use of lift gas



## Monitoring mixing



## Temperature control



ed in its Durban FCCU (a 1952 vintage Model IV, inherited from the Stanvac partnership).

A joint Mobil-UOP effort to commercially develop a new FCC process design started in 1970. In 3 years, ground was broken for a first installation at a Texas City, Tex., refinery. The unit was an early version of the present high-efficiency FCC unit.

The units later installed by Mobil were riser reactors with "shave-off" cyclones, dual feed injection, and high-effi-

## Fluid-unit catalyst inventories smaller

Table 6

	Commercial TCC	Modern riser
Feed rate, 1,000 b/d	18-23	30-150
Total inventory, tons	500-600	150-450
Typical ratio of inventory per 1,000 bbl of feed	30	5

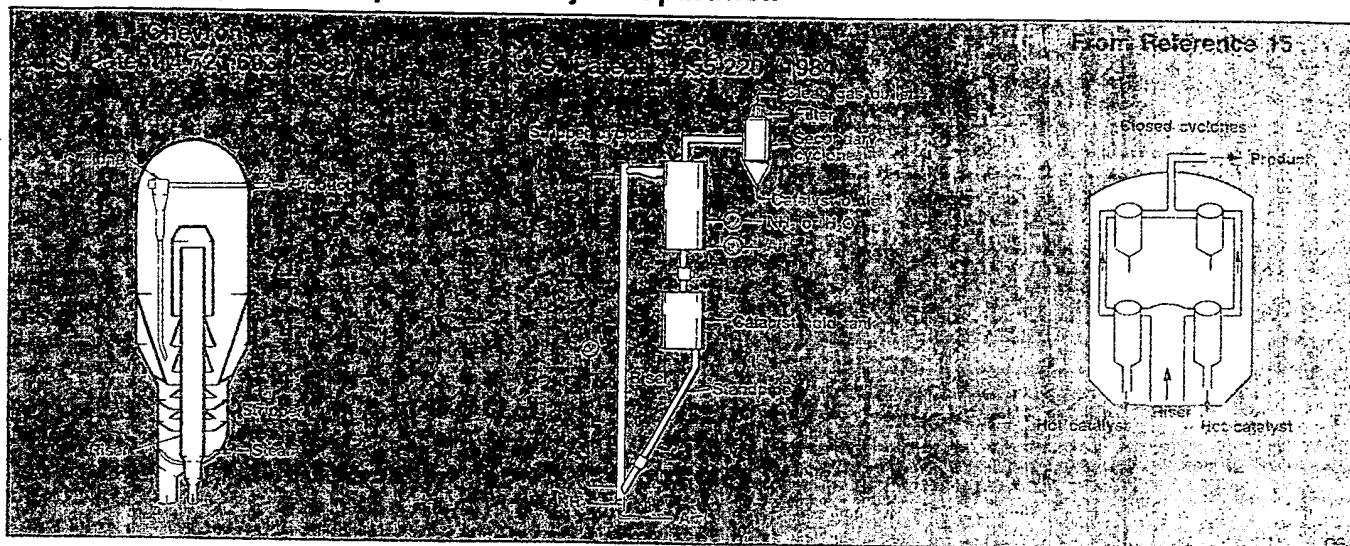
ciency regenerators capable of converting all the CO to CO<sub>2</sub>. These units were capable of fulfilling or exceeding

all of the seven objectives.

After completing the UOP effort, Mobil continued FCC development with quick-sep-



## Examples of quick FCC product-catalyst separation



### How FCC catalysts have evolved

- 1935—Alumina-chloride (Mobil-Gulf)
- 1938—Acid-activated clay (Houdry)
- 1940—Synthetic catalyst (Houdry)
- 1942—Fluid catalyst (Exxon)
- 1943—TCC beads (USY)
- 1946—Microspheroidal catalyst (Davison)
- 1952—D5 zeolite-TCC bead catalyst (SV-Mobil)
- 1954—Spray-dried fluid D5 (Mobil)
- 1957—Fluid USY and REY catalysts (Davison)
- 1974—CO-zeolite catalyst (Mobil)
- 1975—CO-zeolite catalyst (Phillips)
- 1986—ZSM-5 octane additive (Mobil)

### Advantages of zeolite catalysts

	Alumina	USY	X-zeolite
Coke, wt %	12	12	12
Conversion, vol %	55	55	55
C <sub>10</sub> gasoline, vol %	38	38	38
C <sub>10</sub> gas, wt %	6	6	6
C <sub>10</sub> gas, vol %	25	25	25

aration reactor design to eliminate undesirable thermal cracking in the reactor vapor space. This was followed by the development of multi-nozzle feed injectors to enhance catalyst and oil mixing to improve heavy-oil cracking.

Average oil contact times were also reduced as the average feedstock endpoint rose. Reactor temperatures higher than the original goal also became common.

Dust emissions, in recent years, have been controlled in FCC units with a combination of improved cyclone technology and harder catalysts. Mobil developed its own third-stage cyclone tech-

nology to reduce dust emission and to install expander turbines. A bag house or filter is used to clean up this last dust remnant.

Mobil recently installed sintered metal filters in an FCC unit to further reduce dust and lower atmospheric emissions. This technique can be applied to a third-stage separator to virtually eliminate dust carryover to power recovery from flue gas, increasing power recovered and lowering maintenance costs. The initial installation is a Mobil design.

### Catalyst innovations

FCC process development has been driven by catalyst

developments (Table 7). Replacement of ground natural and synthetic catalysts by spray-dried microspheroidal catalysts improved fluidization, reduced attrition, and cut catalyst losses.

The original synthetic amorphous alumina-silica catalysts (10-14 wt % alumina) were replaced by high alumina (25-30 wt %) catalysts.<sup>20</sup> These higher-activity catalysts gave more favorable gasoline-to-coke selectivity, better stability, but somewhat lower octane.

### High-activity zeolites

The introduction of high-activity zeolite catalysts caused a revolution in FCC. Plank and Rosinski (the only oil company representatives in the U.S. patent office Inventors' Hall of Fame) discovered the tremendous boost achieved by incorporating zeolite into a matrix, typically of silica-alumina or clay.<sup>21</sup> (The X and Y zeolites were discovered previously by Union Carbide.)

Zeolite catalysts pushed many units into partial, or all-riser, cracking to minimize coking and gasoline overcracking. Recycle rates were dropped substantially, from 40% in 1965 to below 10% in 1988.<sup>22</sup>

The advantages of zeolite over amorphous alumina catalyst at the same coke yield in a TCC application, are shown in Table 8 and in Fig. 20.

The introduction of zeolite catalysts had the largest single impact on FCC process design and operation. A more recent direction, for octane enhancement, has had more modest operating impact.

### Octane enhancement

The octane of FCC gasoline can be increased by raising riser top temperature. The rule of thumb is 1 research octane number increase per 10° C. increase in temperature.<sup>23</sup>

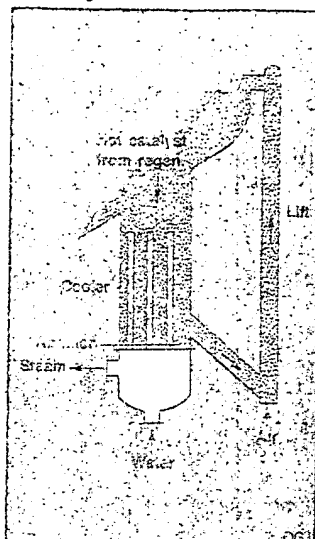
However, gasoline may overcrack to dry gas as well as to alkylation feeds, and the FCCU can run into catalyst circulation, gas compressor, feed preheat, or reactor-metallurgy limits. Catalytic approaches to octane enhancement include the resurfacing of ultra-stable Y zeolites (USY), of high Si/Al ratio and low unit cell size, and use of ZSM-5 additive.

USY catalyst restricts hydrogen transfer reactions, which tend to reduce gasoline octane on standard rare-earth Y (REY) catalysts by producing lower-octane paraffins.<sup>24</sup> Aromatics formation on REY catalysts is offset by higher degrees of polynuclear condensation and coke formation.

The amount of octane enhancement over USY catalyst depends on the degree of dealuminization, sodium content, and amount of rare earth exchanged on the zeolite. These can be monitored

Fig. 33

### Catalyst cooler



### U.S. FCC and HDC capacity growth

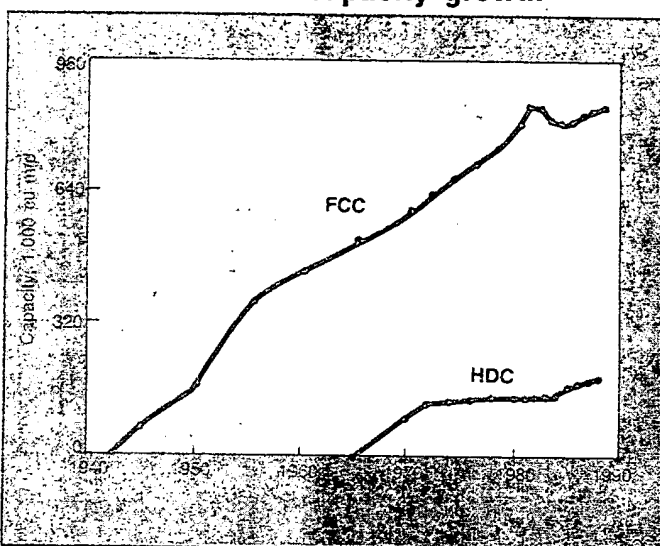


Fig. 34

### Growth in FCC throughput

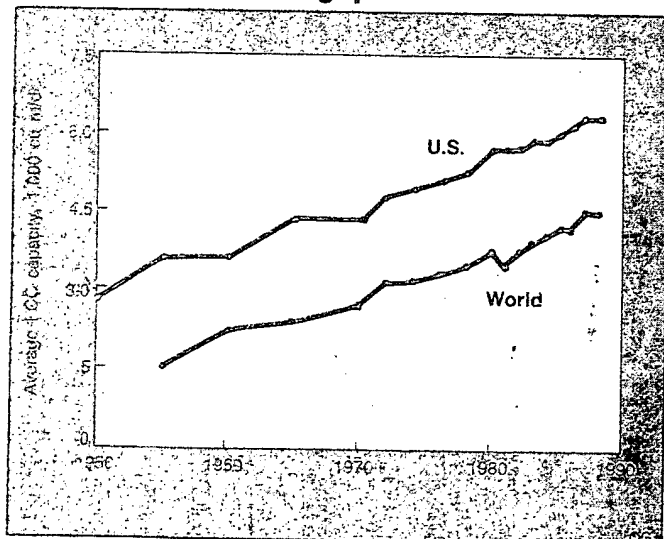


Fig. 35

by their impact on unit cell size, which is lower for zeolites of higher Si/Al ratio, and declines to an equilibrium value dependent on catalyst composition.

For example, rare earth content increases the equilibrium cell size. Pine and co-workers show that octane increases linearly with decreasing unit cell size.<sup>25</sup> However, C<sub>3</sub>—dry-gas make also increases.

USY catalyst is expected to produce less coke and higher-octane gasoline, but at a cost of higher gas make and lower gasoline yield.

Shape-selective zeolite, ZSM-5, converts low-octane components in the back-end of the gasoline to light olefins

(Fig. 21). If alkylation capacity is available, the light olefins can be converted to alkylate, increasing the octane advantage further.

Because dry gas and coke makes are unaffected, ZSM-5 often offers a more favorable route to enhanced octane than raising riser top temperature.<sup>26</sup> A review of catalyst development at Exxon has been published recently.<sup>27</sup>

### Market, regulations

FCC has been called a mature technology by many, probably as far back as the 1950s. But the continuous evolution in catalysts, hardware, process conditions,

and process control proves otherwise.

FCC has constantly gained in importance, and for most refineries, the FCC unit is the key to profitability. For many refineries, FCC has meant staying in business.

The number of U.S. refineries has been steadily declining, as smaller refineries close down. There were nearly 500 refineries in operation in the 1930s.

From 1973 to 1988 the number of operating U.S. refineries declined from 247 to 182, while the number of FCC units has remained constant at 125.

FCC is not a mature technology today, and is not likely to become one in the near future. While hydrocracking will probably offer more competition for new heavy-ends upgrading, FCC will retain its prominent position. FCC units now face many challenges brought about by environmental regulations, product quality demands, and economics.

### Product quality demand up

Gasoline octane has been a major indication of gasoline quality since the 1930s. While octane is only one measure of gasoline quality, it is the one that is heavily advertised.

As we have seen, gasoline octane was a major driving force in Houdry's development of catalytic cracking. Periodically, an "octane war"

has broken out, whether driven by real engine demands, or by marketing pressures.

We are currently experiencing another octane war in the U.S., started by the gradual removal of lead from gasoline and the increase in consumption following the 1986 price drop.

FCC naphtha is not a finished product, but rather a gasoline-blending stock, after stabilization and treatment. FCC gasoline makes up 35% of the gasoline pool (an additional 10% of the pool consists of alkylate from FCC by-products).

Cracked gasoline octane was high in World War II, when cracked gasoline was mainly used as an aviation gasoline-blending stock. Octane decreased after the war but increased again in the 1950s.

Some of the more recent variations in cracked gasoline octane are shown in Fig. 22.<sup>24</sup> Cracked gasoline octane numbers have steadily decreased since 1968, with wider use of zeolite catalysts and crude price increases (which favored higher gasoline yields).

Research octane number has increased in recent years with increasing FCC riser top temperatures (Fig. 22 is normalized to a constant temperature of 500° C.), and increasing use of octane-enhancing catalysts. These catalysts are less successful in increasing motor octane number though, and currently motor octane has probably surpassed research octane in importance to many refiners.

Another important octane feature of cracked gasoline is the variation in composition and octane throughout its boiling range. Typical distributions are shown in Figs. 23 and 24.<sup>24</sup>

Front-end octane, due to C<sub>5</sub> and C<sub>6</sub> iso-olefins, has been an important feature of FCC gasoline. Recent competition to FCC in this range is isomerized C<sub>5</sub> and C<sub>6</sub> paraffinic fractions, which have less octane sensitivity (the spread between research and motor octanes).

**Regulations push FCC**  
Other trends affecting FCC

operation include current or proposed regulations on gasoline volatility (gasoline Rvp is forecast to come down by 2.5 psi in the U.S. by 1992), sulfur, benzene, and possibly aromatics levels.

FCCU's produce additional products other than naphtha. Typical yields for major products are shown in Fig. 25.

The second largest valuable product is light cycle oil (LCO), which can be upgraded to distillate by hydrodesulfurization. In the U.S., considerable amounts of LCO are hydrocracked to increase gasoline yield further. In some other locations, LCO can be a more valuable product than naphtha, and several FCC units are operated to maximize LCO production.

Heavy fuel oil is usually used for bunker fuel, after removal of catalyst fines. Fuel gas, at the other end of the spectrum, is usually desulfurized and consumed in the refinery.

The recent trend toward increasing FCC riser top temperature has almost doubled  $C_4$ -light-ends production, and many FCC units have been experiencing hardware limits (for example a wet-gas limit). Occasionally, a refinery's fuel-gas balance has limited cracking severity.

Many projects to improve heavy and light-ends utilization have been commercialized in recent years. These include fuel-gas separation into components such as ethylene, especially when a refinery is in proximity to a petrochemical producer.

Alkylation of LPG components (iso-butane, propylene, and butylenes) has been of great commercial importance and has paralleled cracking development. Catalytic cracking has increased alkylation feed availability.

Other processes for upgrading LPG to gasoline are available. Catalytic polymerization has a long history, and new units (especially for propylene dimerization) are still being built.

Other processes include the recently developed BP-UOP Cyclar process which can convert paraffinic LPG feed to aromatics.

Current challenges in FCC

technology are driven by product quality, which in turn is driven by market demands and by government-mandated regulations. These product demands exist in a competitive refinery environment of low margins and fluctuating crude prices.

FCC units have been proving their remarkable flexibility by meeting octane demands, while processing lower-quality feeds. These objectives are being achieved at relatively low cost by constantly improving FCC catalysts and hardware.

Hardware and catalyst changes tend to be incremental, and sometimes the improvements seem small. However, even a small increase in gasoline yield or octane translates to a large sum when multiplied by the FCC capacity in place.

### FCC hardware changes

The use of heavier feeds has precipitated a host of innovations in FCC unit hardware. Much of this effort has focused on regenerators and feed injection systems.

Other hot areas include quick quenching of the reaction and faster separation of catalyst from reactive vapors in reactor and stripper.

### Feed injection

The goals of feed nozzles are rapid feed vaporization and uniform mixing with the regenerated catalyst. Multiple nozzles have been preferred for some time over single nozzles.<sup>28</sup> The improvement is shown in Figs. 26 and 27.

Atomizing devices are often used in feed nozzles to generate droplets smaller than 100  $\mu$  (Fig. 28). This helps to spread the feed more uniformly across the catalyst suspension, and it reduces vaporization time.

The nozzles extend into, or beyond, the region of regenerated catalyst entry to the riser. Catalyst can be pre-accelerated prior to oil contact with steam or hydrocarbon gas injected at the base (Figs. 29-31).

Monitoring mixing efficiency and mixed temperature control often yield tangible benefits in fine tuning FCCU

performance. Inclined regions or bends in risers promote catalyst segregation, so vertical risers are favored.

Short contact time in close to plug-flow operation limits coke yield, dry gas make, and gasoline overcracking.

High amounts of dispersion steam enhance feed vaporization, reduce hydrocarbon partial pressure and contact time (less coke), and remove heat. Costs of steam production and recovery, however, restrict the amount of steam available.

Reduction in riser diameter above the mixing zone also reduces contact time and overcracking.<sup>29</sup> The importance of rapid flash vaporization, and a uniform mix temperature has been noted.<sup>30</sup>

Injection of liquid hydrocarbons downstream of the mixing zone has been proposed to shorten the time hot catalyst is in contact with products.<sup>31</sup> If the quench stream adds less coke load than consumed in its vaporization and cracking, it can aid the heat balance with heavier feeds.

### Separation technology

Following the riser, the separation of product vapors from catalyst and from hot reactor vessel walls has generated considerable interest (Fig. 32). Stripper cyclones, closed cyclones, and other techniques have been proposed to prevent overcracking, catalytically or thermally.

The remaining vapors entrained with down-flowing catalyst are stripped by countercurrent steam. High length/diameter ratio, unbaffled, staged stripping is one suggestion for heavy-oil feeds.<sup>32</sup>

### Regeneration improvements

External catalyst coolers are becoming popular hardware options to reduce regenerator heat load, and to allow for processing of heavier feeds. Steam tubes have been used in some FCC regenerators, but offer limited turn-down capacity.<sup>14</sup>

External catalyst coolers in catalyst recirculation lines have received considerable attention. Some are updates of older, low-density, upflow exchangers, with solids circu-

lation regulated by slide valve.<sup>33</sup>

Current designs (Fig. 33) use dense-phase downflow of solids, controlling heat removal by adjustments in aeration to the exchanger, which directly affects catalyst-side heat transfer. Catalyst returns to the regenerator through a lift line, and circulation depends on relative densities in the cooler loop, without use of a slide valve (as in Model IV circulation loops).

Other regenerator modifications have the goals of higher combustion efficiency, reduced pollutants emissions, and reduced catalyst inventory. Mobil pursued these goals with the Mobil-UOP high-efficiency regenerator.

Addition of a second regeneration stage to process heavier feeds provides these advantages.<sup>31</sup>

- First stage burns 70% of the coke, and most of the hydrogen, at a maximum temperature of 700° C. The low temperature and incomplete burn-off of carbon limit catalyst deactivation from steaming.

- Catalyst is transferred to a second stage of regeneration, but the first-stage flue gas, with its high steam partial pressure, is vented.

- The second stage can operate at high temperature (above 800° C.) in a dry environment of excess air, burning the catalyst clean with a minimum amount of hydrothermal deactivation.

### FCC gains strength

Following a dip through the first half of the 1980s, U.S. FCC capacity resumed its ascent (Fig. 34).

Moving-bed cracking capacity (TCC and Houdrflow) has continued to decrease to a point where very little capacity is running today. Average FCCU capacity continued to increase (Fig. 35), with the U.S. having larger units than the rest of the world. (Single unit capacities range from 2,000 to 150,000 b/d.)

### Hydrocracking up

Hydrocracking, a long-term competitor to FCC, has been increasing in importance



## U.S. vs. Western Europe product demand

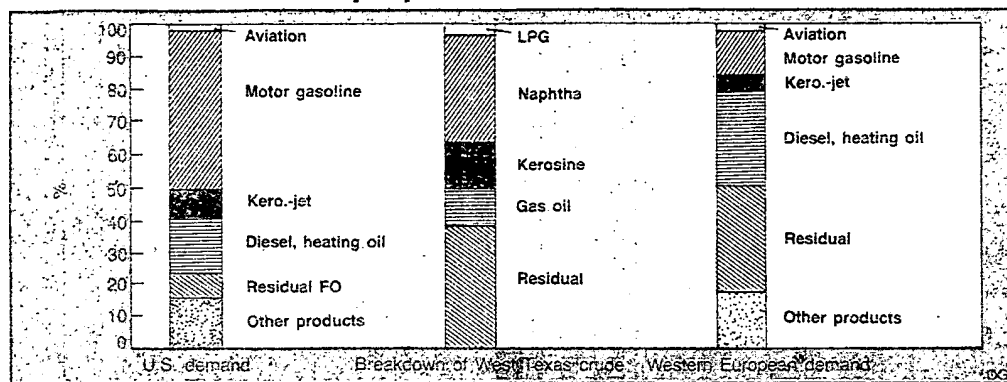
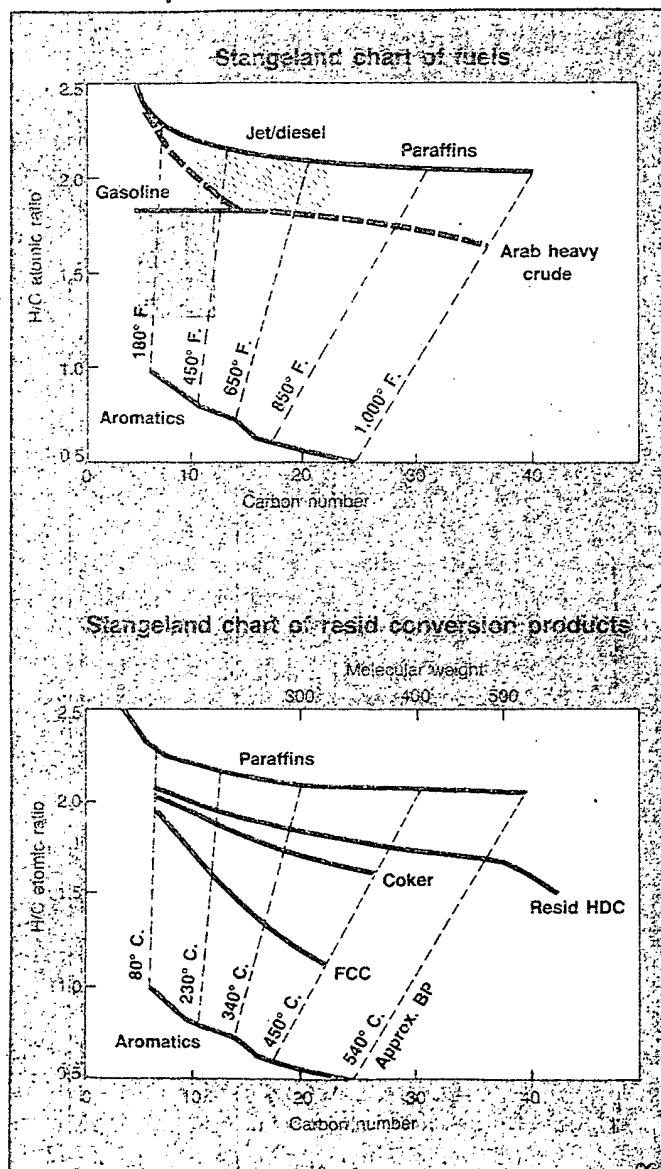


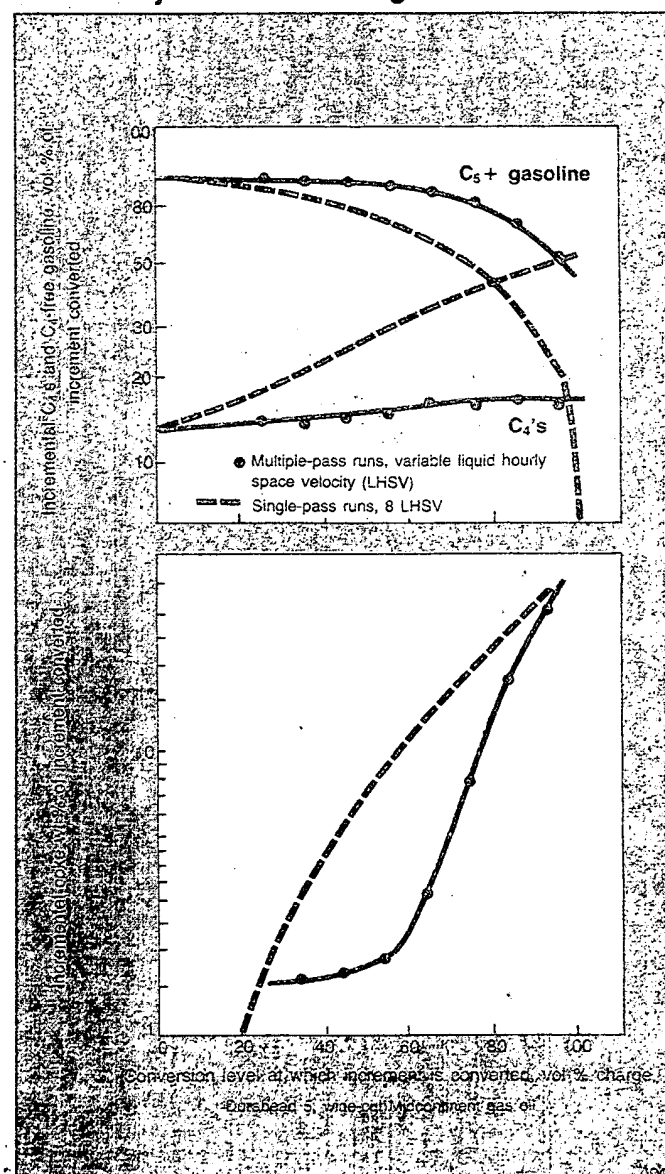
Fig. 37

Fig. 38

## Increased product H/C ratio needed



## Ultimate yield in cracking over zeolite



slowly. Historically, there has always been a connection between hydrocracking and catalytic cracking.

Hydrocracking of petro-

leum fractions would have probably been commercialized in the 1930s, following development of the Bergius Coal Hydrogenation process

in Germany, were it not for the persistence of Eugene Houdry in developing catalytic cracking. Hydrocracking was finally commercialized in

the 1960s, but the revolution in cracking brought about by zeolite catalysts slowed its expansion.

Hydrocracking has come

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Owen

into its own now and is challenging FCC. In many refineries, the two processes have been integrated to complement each other.

Fueling the expansion in cracking capacity over the past few decades is the discrepancy between crude oil composition and market needs. U.S. demand requires almost 50% of the petroleum barrel as motor gasoline, at a ratio of about 2:1 of gasoline to distillate.

Other countries need less than half this amount of gasoline, but twice as much distillate. Fig. 36 contrasts the demand structure in the early 1970s in the U.S. and Western Europe to a typical West Texas crude.<sup>23</sup>

There is a need for increased product hydrogen-to-carbon (H/C) ratio, achieved by carbon rejection (coker or FCC) or hydrogen addition (HDC). The Stangeland charts in Fig. 37 show these options for residuum.<sup>34</sup> Disposal of the bottom of the barrel is occasionally pursued in cracking units. Catalytic cracking rejects less carbon than coking, and net liquid yields and product quality are higher.

### More resid cracking

From the early years of petroleum refining, converting the entire residuum fraction to valuable light product has been a constant, though elusive goal. In 1914, Friedrich

Bergius succeeded in hydrogenating heavy oils to gasoline at 430° C. and 120 atm.<sup>4</sup>

These efforts led to the commercialization of coal hydrogenation. As early as 1909, Burton and Humphreys were experimenting with thermal cracking of residuum, at high temperatures and at as high a pressure as they dared, at the Whiting, Ind., refinery of Standard Oil Co. of Indiana.

The Burton process became a major commercial success in 1913, after Burton realized that leaving out the heaviest fractions was the key to a successful process.<sup>3</sup> Heavy petroleum fractions have continued to be used in other thermal processes, such as coking and visbreaking, and for the manufacture of lubes, asphalt, and residual fuels.

The old dream of converting those heavy ends to gasoline has been pursued over the years and, since 1979, we have seen a resurgence of interest in resid upgrading. Trends in resid processing are tabulated by Davison Chemical Division of W.R. Grace & Co.<sup>35, 36</sup> The definition of resid in the surveys extends to any operations with over 5 vol % of the feed boiling above 1,000° F.

Initial growth in resid processing in the U.S. was rapid, jumping from 23 FCC units in February 1981 to about 52 in October the following year. The survey in 1987 reported almost no change since, with 53 FCC's charging resid. This is about 40% of U.S. FCC capacity.

Two features were typical for FCC units cracking resid: lack of alternate disposal processes (such as cokers), and location. Units that are located inland, with poor fuel oil markets, or those on the East Coast with easy access to good-quality resids, have higher reported resid usage.

The economic driving force for resid disposition in FCC will pick up again in the coming decade if crude oil prices increase significantly.

The major challenges to the refiner for resid use in FCCU's are:<sup>37</sup>

- High residual carbon in resid (median Conradson

carbon residue, CCR, of all U.S. FCC feeds was 1.1 wt % in 1987; for resid processors it was 5.7%).

- High metals content (3 ppm Ni+V average vs. 12 ppm for resid).

- High heteroatom content.

The first challenge would severely restrict conversion in a typical heat-balanced FCC, leading to extreme regenerator temperatures (rapid catalyst deactivation) and low catalyst circulation rates (reduced conversion). Approaches to debottleneck FCCU's include low-coke make catalysts, increased air blower capacity, and catalyst coolers. Staged regenerators have also been installed.

Feed metals are detrimental for two reasons: nickel, in particular, increases hydrogen and coke yields, and vanadium to a lesser extent. And vanadium (also sodium) degrades zeolite structure.

The large dry-gas volume associated with even small H<sub>2</sub> yields affects downstream gas compression considerably. Accelerated catalyst makeup, use of good quality purchased equilibrium catalyst, or low-cost "flushing" catalyst, have been suggested as ways to reduce metal loadings.

Another popular approach has been metals passivation. Phillips Petroleum Co. licenses the use of antimony, cutting nickel dehydrogenation roughly in half. Other nickel passivators, such as bismuth, have been patented.

Techniques for vanadium passivation are also pursued, tending toward use of vanadium traps, or sinks, to prevent its destructive interaction with the zeolite.

Heteroatom concentration in the resid impacts both process and environment. Basic nitrogen compounds in the feed strongly adsorb on catalyst acid sites, adding to the burning requirement and contributing to regenerator NO<sub>x</sub> emissions. Catalyst activity is reduced, although it is regenerable.

A portion of the additional resid sulfur will be carried to the regenerator, increasing SO<sub>x</sub> emissions. Catalyst technology is available to carry at

least some of the sulfur oxides back to the riser where they are reduced to  $H_2S$ .

The sulfur oxide capture function can be incorporated into the cracking catalyst, or added separately. The reaction is favored by higher sulfur oxidation states, and typically is combined with excess regenerator oxygen for maximal  $SO_x$  reduction.

### Challenges ahead for FCC

It is tempting to assume that there are no remaining quantum improvements in catalytic cracking. This was probably the opinion in the decade before zeolites came on the scene.

#### Higher gasoline yield

A 1965 pilot by Mobil researchers Farber, Payne, and Sailor (Fig. 38), based on TCC zeolite catalyst, shows how far we still are from what might be considered ultimate yields in catalytic cracking.

Running at low conversion per pass with intermediate gasoline removal results in much higher gasoline selectivity than single-pass conversion. The cumulative advantage increases with conversion: 13% more gasoline at 60% conversion, and 24% more at 80% conversion.

The results of multipass runs show much lower coke and light gas yields than single-pass operation. Coke can be produced from condensed and polymerized hydrocarbons formed from reactive intermediates.

Coke and light gases can result from cracking of gasoline product. While using zeolite catalysts reduces coke formation due to steric hindrance, compared with amorphous catalysts, it does not eliminate it. There remains considerable potential for increasing FCC gasoline yields.

We believe that FCC technology, operating conditions, and apparatus are going to be as similar and as different 50 years from now as today's technology is compared to the Model I. Many basic principles will probably be retained, but the evolutionary process which has been responsible for past progress

will continue. Yet, there is room for real breakthroughs.

#### Possible breakthroughs

Two possible areas are high-activity, high-temperature, once-through cracking<sup>11</sup> and very short contact time cracking.

Contact time in cracking has been steadily reduced with improvements in catalysts to current state-of-the-art risers with oil residence times as low as 1 sec. There may be incentive to reduce contact times further, and residence times lower than 1 sec may become a commercial reality.

The pioneering work of Bergougnou and coworkers in "ultra short contact time" pyrolysis shows the feasibility of one such reactor for non-catalytic applications.<sup>38</sup> A similar concept, demonstrated on a 250 b/d scale, is Stone and Webster's "Quick Contact" (QC) process.<sup>39</sup>

The art and science of fine-powder fluidization was created along with FCC, and much of subsequent interest in fluidization has been due to FCC. Yet, basic understanding of complex fluidization phenomena is almost completely lacking.

Even reliable empirical correlations of entrainment, slip velocity, etc., leave a lot to be desired. While it is true that many FCC licensors and operators have a large body of in-house proprietary data and correlations, some of these are not adequate, and fail when extrapolated beyond their data base.

Industry cooperative groups, such as Particulate Solids Research Inc. (PSRI), have greatly contributed to filling this void in reliable correlations for their member companies. But research in academia seems to be neglecting multi-phase phenomena, including fluidization.

Not only is practical fluidization suitable for academic research, but it can shed light on largely unexplained basics. We urge members of academia not to pay too much heed to those proclaiming the untimely death of classical chemical engineering.

While research in biochemical and super conductivity is

becoming an exciting part of chemical engineering, it should be complemented by research in traditional fields. We believe fluidization and FCC are as glamorous and as high-tech as the new areas. They were in the past, as this review has shown, and will be even more so in the future.

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